Thermal Decomposition of Toluene at Intermediate Temperatures in the KSU Single Pulse Shock Tube

by

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I would like to dedicate the present work to my parents for their effort to provide me with an education and a respectable place in society.

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Finally, but not because it represents the least, to the one who has given me the most support during these years as a graduate student, my wife Chris.

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1.0 INTRODUCTION

1.1 Problem Formulation and Engineering Significance

Mankind has been using organic fuels for industrial and domestic purposes for many years. The fluctuating price of petroleum and the numerous hazards involved in the inefficient combustion of fossil fuels have motivated the diversification of fuel sources as well as the U.S. Government and private companies interest for new research involving the causes of inefficient combustion in some of the most widely used hydrocarbons. Extensive and recent research on fuels such as benzene, acetylene, cyclohexane etc. has demonstrated that soot formation is a problem in the combustion of hydrocarbons. This problem results in: 1) environmental hazards from emission of particulates and associated compounds, 2) engineering difficulties in the materials due to the thermal radiation from soot particles, and 3) mechanical or heat transfer hindrance caused by layers of soot deposited on critical surfaces within a mechanical device.

The environmental hazards that soot represent are very well known. Early papers in medicine such as the one published in England by Sir Percival Pott in 1775 discussed the cancer of the scrotum as an occupational disease of chimney sweeps.[1] These chimneys contained deposits of soot formed from the burning of coal. More recent studies have confirmed that solid particles from coal and oil-fired power plants contain a large number of carcinogenic compounds. The identification of carcinogenic compounds in soot has yielded a large list of benzene extractable polycyclic aromatic hydrocarbons (PAH).

A second problem that the emission of soot represents is the engineering difficulties caused by the thermal radiation of soot particles. An example of this is discussed by Vaughn[2] who reported that soot particles accumulate in the blade section of an advanced design high temperature gas turbine and cause detrimental effects by the increase in temperature due to the thermal radiation from soot particles.

Finally, another problem where soot formation can be held responsible is the mechanical or heat transfer inefficiency of mechanical devices by soot proliferation on critical surfaces.

All of these undesirable consequences of soot formation have produced a special interest in the pyrolysis of aromatic hydrocarbons for the present research work, where toluene waa chosen to increase our understanding of the initial steps involved in the production of soot.

1.2 Thermal Decomposition of Toluene

The present section gives a brief description of the experimental work performed on toluene pyrolysis. The discussion format starts with a background information about toluene; then, special attention is given to the different experimental studies on toluene pyrolysis reported in the literature.

The diacovery of toluene goes back to the mid 1830's when Pelletier and Walter[3] were able to obtain this product by heating rosin oil, and later on, Deville[4] reported his results on the distillation of the Balsam of Tolu, a natural resin shipped to Europe from the seaport of Tolu in Colombia, South America.

Toluene was officially recognized as a new hydrocarbon later in 1847, when Charles Mansfield separated this product and some others from coal tar.[5] Despite the fact that toluene was quickly recognized as a good solvent, significant commercial use did not occur until it was realized that the nitration of toluene would produce T.N.T. (Tri-nitro-toluene), a very powerful explosive. It is also a solvent for paint and ink and used in printing newspapers and magazines. One of its most important applications came with the invention of the internal combustion engine where it has been used with other aromatic hydrocarbons in gasoline to suppress engine knock, thereby increasing the power and providing a smoother running engine.

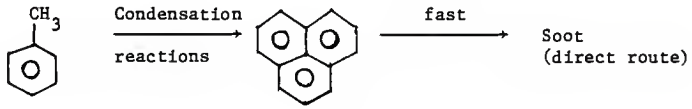
Toluene pyrolysis has been a subject of interest in combustion studies. These studies can be divided into three different areas due to the treatment that experimentalists have given to its pyrolysis: 1) soot formation studies, 2) kinetic studies, and 3) product yield studies.

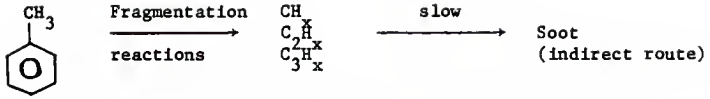
1.2.1 Soot Formation Studies

Studies on soot formation from toluene pyrolysis are relatively a new subject that experimentalists have been concentrating on due to the similarity in the soot yields with other aromatic hydrocarbons (such as benzene). Three theories on soot formation from pyrolyzed hydrocarbons

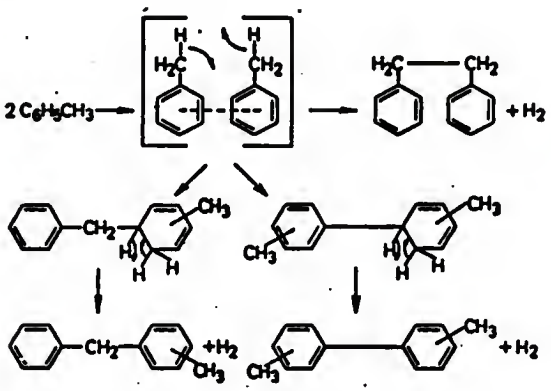
have been proposed from studies as early as 1953.[6,7] These theories are also discussed by Vaughn[2] and they are: 1) The acetylene theory, which proposes that a decomposed hydrocarbon forms unsaturated fragments (such as acetylene) that polymerize and produce larger species that eventually form soot. 2) The C_2 polymerization theory, which proposes that the pyrolyzed hydrocarbon forms C_2 intermediate fragments that represent nucleation sites for polymerizations with other species or the C_2 themselves polymerize to form soot. And finally, 3) the polymerization theory that proposes a series of polymerization reactions to form a high molecular weight polymer that dehydrogenates to form soot particles.

A general mechanism that most authors have adopted has been the one proposed by Graham, et al.[8] working with a shock tube in the high temperature region 1600-2300 K (reaction time 2.5 msec). Experiments with benzene, toluene, ethylbenzene and indene, highly diluted with argon led to the conclusion that soot is formed from aromatic hydrocarbons in two different pathways: 1) a direct fast route, with condensation reactions and almost instantaneous soot formation at temperatures below 1750 K, and 2) an indirect slow route from the hydrocarbon fragments produced at high temperature. This mechanism is shown below and it condenses the three proposed theories for soot formation outlined earlier.





Although Graham, et al. considered that temperature was the determinant parameter for the soot formation, other studies have proved that reaction time is also a parameter of important consideration in the proposal of soot formation routes. For instance, Fields and Meyerson[9] pyrolyzed toluene and toluene-α,d_3 at low temperature (873 K) and large contact time (6 sec). They proposed a bimolecular complex via such reactions as



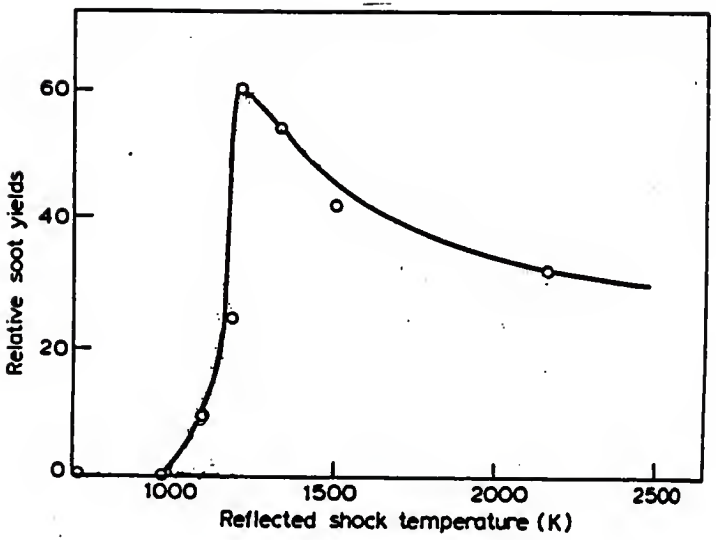
where toluene can form bibenzyl via dihydrogenation or can collapse to a benzyl-or tolyl-methyl cyclohexadiene which loses hydrogen to yield methyldiphenylmethane or dimethylbiphenyl. Similarly, Kershaw[10] in 1978 working in a rotating autoclave at low temperatures (623 K - 723 K) and long reaction times (1-3 hours) found a high concentration of bibenzyl, diphenylmethane and methylbiphenyl together with three isomers of bibenzyl, which are also soot precursors. In the present work, it

will be seen later that these high molecular products were observed in lower concentration due to the low reaction time.

In 1981, Evans and Williams[11] working with shock tube and mixtures of toluene and argon (C:Ar ratio 0.01:1) reported soot yield curves for the temperature range 715-2159 K where the soot yield was zero at around 1000 K, increased to 60% at 1200 K and then decreased to 30% at around 2200 K (see Fig. 1). The reaction time in this study was not reported, but from results in the present study it is presumed to be much greater than 2 msec. Evans and Williams agreed with the mechanism for soot formation proposed by Homann and Wagner[11] that consisted of the step-wise addition of C_2 radicals of acetylene to form polyacetylenes. The polyacetylene radicals combine with other polyacetylenes to produce large branched radicals. The acetylene radicals are formed from the pyrolysis of acetylene and ethylene.[12]

Studies on soot formation from toluene by Wang, Matula and Farmer[13] using a shock tube (1981) produced some new and interesting results. They concluded that condensation, polymerization and dehydrogenation are the most important soot formation steps not only for toluene but also for other fuels, and fragmentation seemed to have a less important role. From their experimental results they also concluded that at temperature lower than 1800 K an increase in toluene concentration increased the soot yields due to an acceleration of the condensation process. Hydrogen and oxygen were introduced to the system, and it was observed that an increase in oxygen or hydrogen concentration in the toluene/argon mixture would decrease the soot yields. At low temperature, the suppression effect of oxygen (or

Fig. 1. Variation of relative Soot Concentration with Temperature during the Pyrolysis of Toluene. (Evans and Williams).[11]


Relative soot yields
60
40
20
0
1000
1500
2000
2500
Reflected shock temperature (K)

hydrogen) in soot formation was smaller than at higher temperature, this was explained by Wang, et al. arguing that the oxygen (or hydrogen) molecule attacked the methyl group at low temperature allowing for condensation of phenyl groups to form soot. However at high temperature, oxygen would attack the phenyl radical suppressing the soot formation.

The latest studies of soot formation from toluene were performed by Frenklach et al.[14,15] in 1983 and 1984. In these studies, the combustion of toluene and oxygen mixtures in argon was observed behind reflected shock waves in the temperature range 1496-2391 K and pressure range 1.85-3.04 atm. The mol fraction of toluene in argon was changed from 3.11×10^{-3} to 1.75×10^{-2} and the toluene/oxygen ratio was maintained at one. The results ratified earlier studies by Wang, et al. where they found that an increase in toluene concentration at low temperature increased soot yields. However, Frenklach et al. explains this behavior by stating that "addition of oxygen causes reactions to occur that compete with pressure-dependent fragmentation of the aromatic ring" which is similar to the physical explanation given by Wang et al.

Also, Frenklach et al. presented an empirical modeling of soot formation[15] for given reaction times at various temperatures, pressures and initial reactant concentrations which could be used for different fuels. The model included fragmentation and polymerization processes, and soot yields from toluene/argon mixtures given the following conditions:

Temperature range:	1500-2400 K
Pressure (P_5):	2.05 to 2.98 atm
Time:	0.5_3- 2.0 msec.
Toluene mol fraction in Argon:	10^{-3} to 10^{-2}

The results for three different cases: pressure dependence, variation of reaction time and concentration dependence, were compared to experimental results and the predictive power of the model was in good agreement with the experimental data. Figure 2 shows the experimental data and predicted results from the model.

1.2.2 Kinetic Studies

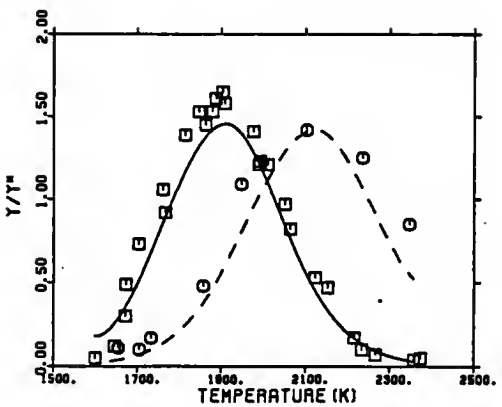
The earliest kinetic studies in toluene pyrolysis performed by Tilicheev (1939) and M. Swarc (1947)[39] reported values for the bond energy of the C-H bond of 293.1 kJ and 324.5 kJ respectively. Also, Swarc found that the reaction is of first order by changing the contact time and the toluene pressure in the system. The kinetic rate constant that he reported for the initial step reaction in toluene decomposition

$$C_7H_8 \longrightarrow C_7H_7 + H\cdot \qquad (1.1)$$

was $K_1 = 2.0 \times 10^{13} \exp(-324.5\ (kJ)/RT)\ sec^{-1}$.

A higher value for the C-H bond energy was reported by H.R. Anderson, et al.[16] as 374.7 kJ at room temperature working on the bromination of toluene. However, the discrepancy with early results from Swarc was not discussed and was only left to future studies on this matter.

Fig. 2. Experimental Data and Predicted Values from Empirical Model for Soot Formation from Toluene by Frenklach, et al.[15]
(a) Constant reaction time, varying concentration and Pressure.
(b) Constant concentration, varying reaction time.
(c) Constant reaction time, varying concentration.

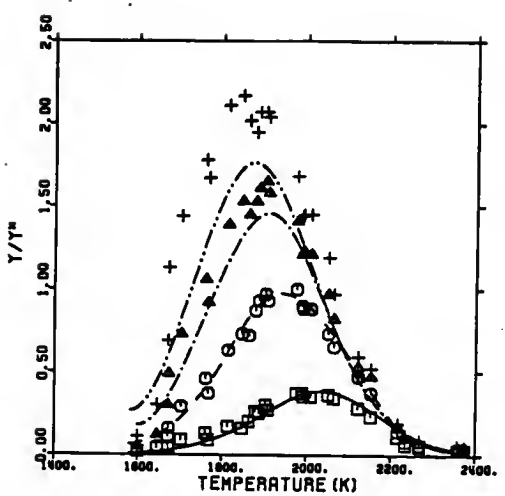


Time: 1.0 msec, Concentration: 0.311% C_7H_8-Ar: □

1.75% C_7H_8-Ar : ○

The lines are computed by model at corresponding conditions.

(a)



Concentration: 0.311% C_7H_8-Ar, Time: 0.5 msec: □

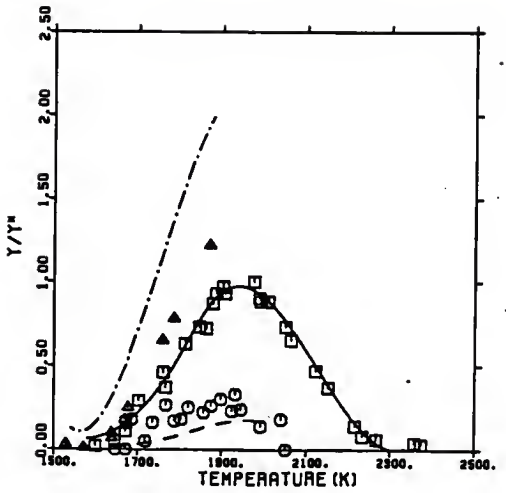
1.0 msec: ○

1.5 msec: △

2.0 msec: +

The lines are computed by model at corresponding conditions.

(b)



Time: 1.0 msec, Concentration: 0.10% C_7H_8-Ar : ⏲

0.311% C_7H_8-Ar: ⏍

1.00% C_7H_8-Ar : ⚠

The lines are computed by model at corresponding conditions.

(c)

Kinetic studies by Blades, Blades and Steacie[17] were not consistent with previous observations by Swarc. This newer study found that the first order rate varied with pressure, contact time, and the experimental surface reactor vessel. An activation energy of 376.8 kJ and a frequency factor of $10^{16.0}$ were reported, so postulation of the equation

$$C_7H_8 \longrightarrow C_6H_5 + CH_3\cdot \qquad (1.2)$$

with reaction (1.1) was assumed to be possible. This postulation and the deviation from first order behavior made it "impossible to assign the observed activation energy to a specific step in the process."

Experimental results from M. Takahasi[18] found the log K_1 vs 1/T plots to be concave (K_1 is the first order reaction rate constant), therefore, the temperature range (1011-1206 K) was divided into two regions. It was observed that the reaction rate constants for the two temperature regions varied as contact time, volume and surface area of the reaction vessel were changed. This behavior was presumed to be due to the suppression of any unfavorable secondary reaction; however, there was no experimental evidence that supported this theory. Takahasi then discussed three possible causes of the concave behavior in the log K_1 vs. 1/T plots: 1) experimental errors of the small amount of products present at lower reaction temperature, 2) correction used for reaction rate constant using a more elaborate Arrhenius form

$$K = A\ T^n \exp(-E/RT) \qquad (1.3)$$

where A is preexponential term, T is temperature, n is a temperature

correction factor assumed to be 0.5, E is energy of activation and R is the universal gas constant, and 3) complications arising from competing reactions with different activation energies.

In 1961, Price[19] found that the first-order rate constants decreased approximately 9% when the contact time was reduced from 1.0 to 0.41 seconds. The reaction rate constant for reaction (1.1) was found to be $K_1 = 10^{14.8} \exp(-347.5\ (kJ)/RT)\ sec^{-1}$.

In 1971, Peacock, Brooks and Cummins[20] working with a static system reported a value of $K_1 = 10^{15.96} \exp(-372.2\ (kJ)/RT)\ sec^{-1}$ for reaction (1.1) and an estimate for the reaction

$$C_7H_7 + H_2 \longrightarrow C_7H_8 + H\cdot \qquad (1.4)$$

of $K_1 = 10^{9.45} \exp(-60.7\ (kJ)/RT)\ sec^{-1}$ was established. Energies of activation for the formation of hydrogen and methane were also reported as 309.8 kJ/mol and 374.3 kJ/mol respectively. The addition of hydrogen to the system accelerated the reaction process.

More recent kinetic studies in toluene pyrolysis performed in the early to mid 1980's include experimental work performed by Troe, et. al.,[21] Banerjee, et al.,[22] and Skinner et.al.[23] Troe working with a shock tube found a limiting high pressure rate constant $K_1 = 8 \times 10^{16} \exp(-380.0\ (kJ)/RT)\ sec^{-1}$ for the temperature range 1100-1800 K. Banerjee et al. reported a value of $K_1 = 10^{8.567} \exp(-186.5\ (kJ)/RT)$ for the range 873-1000 K which he recognized to have a lower activation energy due to "the different experimental conditions and calculation methods used". Finally, Skinner et al. in 1984 using a shock tube calculated a limiting high pressure value of $K_1 = 2.7 \times 10^{14}$

exp (-347.5 (kJ)/RT) sec^{-1} for reaction (1.1) in the temperature range 1000-1800 K. This last paper includes reported rate constant values for other reactions occurring in toluene and deuterated toluene pyrolysis.

1.2.3 Product Yield Studies

This last section in reported toluene pyrolysis studies gives a brief discussion on the product yields observed in previous works.

In 1867, Berthelot[24] found hydrogen, methane, acetylene, benzene, and bibenzyl and other aromatic hydrocarbons with condensed rings. Later in the late 1930's and early 1940's, Tilicheev and Swarc observed bibenzyl as the main product yield, and immediately reaction mechanisms were postulated (see Results and Discussion). Steacie et al.[17] found additional compounds such as styrene, dimethyl biphenyls, and anthracene which were also reported by Takahasi.[18] In 1961, Price[19] observed small amounts of ethylene and ethane. More recent studies performed by R. Smith[25,26] and J.R. Kershaw[10] report the yield of high and low molecular weight compounds. These compounds are shown in Tables 1, 2 and 8. From the studies performed by Smith, it is concluded for the temperature range (1173 - 2073 K) that the highest yield product is acetylene whose yield increases with temperature, indicating the disappearance of all compounds ultimately to form acetylene. Other high yield compounds were methane (whose yield reaches a maximum of 24% at 1573 K), benzene (11% at 1673 K), diacetylene (6.3% at 1673 K), and ethylene (5.2% at 1673 K).

The present study on toluene decomposition was based on results from all these previous studies. The purpose of this research was to

investigate the thermal decomposition of toluene in vapor phase in the temperature range 800 K to 1700 K using a single pulse shock tube. The yields of vapor phase and solid products were measured and a mechanism for the production of the major products was proposed using available kinetic data from the literature.

Table 1. Heavy Species Found by R. Smith (1979)[25]

	Product
C_8H_8	Styrene
C_8H_{10}	Ethylbenzene p-Xylene
$C_{10}H_8$	Naphthalene
$C_{12}H_{10}$	Biphenyl
$C_{13}H_{10}$	Fluorene
$C_{13}H_{12}$	Methyl biphenyl
$C_{14}H_{10}$	Phenanthrene
$C_{14}H_{10}$	Anthracene
$C_{14}H_{12}$	Stilbene
$C_{14}H_{14}$	Bibenzyl Benzyl toluene Dimethyl diphenyl
$C_{16}H_{10}$	Fluoranthrene Pyrene
$C_{17}H_{12}$	Benzofluorene
$C_{18}H_{12}$	Chrysene 1,2-Benzanthracene
$C_{19}H_{14}$	Methylchrysene
$C_{20}H_{12}$	Perylene Benzofluoranthene Benzopyrene

Table 2. Heavy Species Found By Kershaw (1978)[10]

Product
2-Methylbiphenyl
Diphenylmethane
3-Methylbiphenyl
4-Methylbiphenyl
Bibenzyl
4-Methyldiphenylmethane
3,3'-Dimethylbiphenyl
4,4'-Dimethylbiphenyl

2.0 EXPERIMENTAL METHODS AND TECHNIQUES

2.1 Introduction

The pyrolysis of toluene has been studied throughout the years using different techniques. The first reported technique goes back to 1867 when Berthelot[24] passed toluene through a glowing red porcelain tube in which he found similar products to those found in the present work. Later on, Tilicheev in the Soviet Union (1939) and Swarc in England (1947) continued experimental work on toluene pyrolysis using a flow reactor which was a very popular technique used in the early studies of the pyrolysis of toluene and other hydrocarbons.[22,19,18,27,28] Other techniques used in toluene pyrolysis studies were: static systems,[20] laser heating,[29] and shock tube.[23,30,31,32,33]

Following the work performed by Tilicheev and Swarc using flow reactors (and later Takahasi,[18] Blades, Blades, Steacie[17] and Price[19]), Brooks, Cummins and Peacock[20] in 1971 decided to use a static system because they argued that in flow systems the mixture composition could not be varied easily and the reaction time was difficult to measure accurately. Flow reactors were widely used in early investigations due to the fact that the reactant and produced gases were easy to handle and relatively large amounts of gas products could be collected for analysis. However, the availability of modern gas-chromatographic techniques makes these advantages obsolete.[20] Flow reactor techniques in the form of Knudsen cells and rotating autoclaves were later used by R. Smith[25,26] and J. R. Kershaw[10] but

the need for a system that could handle high temperature pyrolysis (flow experiments cannot exceed the softening point of quart[34]) and small adjustable reaction times in the absence of oxygen made possible the use of the shock tube.

Shock tube experiments have been conducted successfully in the recent years in toluene pyrolysis. These studies have been basically intended to observe the behavior of products and radical species in short reaction times with fast cooling periods, and also for the postulation of reaction mechanisms and kinetic parameters when soot particulates are formed or are in the process of formation.

In the present study a Single Pulse Shock Tube (SPST) was used in which the concentration, reaction time, and reaction temperature were prescribed parameters and final species concentrations, overall reaction rate, and kinetic mechanism for vapor phase toluene pyrolysis were to be determined.

2.2 Materials

All the experiments in the present study were performed using Toluene (Grade 99.9) as a reactant, provided by Aldrich Chemical Company. The purity of toluene was checked by gas chromatographic analysis and there were some unidentified C_4 and C_5 impurities that accounted for 0.5%. This toluene was used without further purification. Carbon Disulfide (CS_2-Purified Grade, Fisher Scientific) was used for the extraction of solid products from a liner that fit into the test section.

Accessory equipment used for the shock tube included two mechanical pumps (Duo Seal, Model 1402) and a water cooled diffusion pump (Veeco,

Model EP-2W) that evacuated the shock tube to 1.32×10^{-6} atm. Also a digital oscilloscope (Tektronix, model 76234) connected to a timer (Fluke, model 720012) with two pressure transducers in the test section to record the pressure history and the time for the shock to pass through the test section. The signal from the transducers was amplified by two linear amplifiers (Ortec, model 410) and an Ortec (model 456) HV power supply was also attached to the system. Pictures taken on the oscilloscope were recorded by a Tektronix (model C5B) camera.

2.3 Analytical Instruments

The analysis of all gaseous and solid (or liquid) samples was performed by three gas-chromatographs(GC): Carle (model 311), Perkin Elmer (model Sigma 3B), Tracor (model 560). These analyzers were equipped each one with flame ionization detectors and the Carle GC had the option of a thermal conductivity detector. All three analyzer conditions are shown in Table 3. These analyzers were all connected to a computer (Perkin-Elmer Sigma 15) that recorded the data. Identification of the species present in the compounds was made by injecting known samples and comparing retention times. Quantitative results to yield the concentrations of species in the sample was made by comparing the sample areas from the analyzers with the areas obtained from calibration curves of known species. This is explained in the following equation:

$$C_s = \frac{C_c}{A_c} \times A_s \times \frac{MW_c}{MW_s} , \qquad (2.1)$$

Table 3. Conditions for Gas Chromatograph Analyzers

Analyzer	Interest	Gases Used	Flows or Pressures	Analyzer Temperatures	Column
Carle Series S Model 311	C_1 - C_4	Helium N_2 H_2 Air Zero Grade Union Carbide	60 psig 30 mℓ/min 60 psig 25 psig 18 psig	Column: 57°C Isothermal	2.7% Carbowax 1540 on Porasil C 80/100 mesh 2 7.5% Bix Mix on Chromosorb P-AW 45/60 0.4% Carbowax 1500 on Carbopack B.60/80 mesh
Perkin Elmer Sigma 3B	C_5 - C_6	Air N_2 H_2 Zero Grade Union Carbide	35 psig 20 mℓ/min 18 mℓ/min	Oven: 65°C Inj. Port: 125°C Fid: 125°C Isothermal	10% TCEP mesh 80/100 Chromosorb by Supelco Glass
Tracor 560	C_7 - and up	Air N_2 H_2 Zero grade Union Carbide	400 mℓ/min 25 mℓ/min 30 mℓ/min	Oven: 150°C Inj. Port: 200°C Fid: 200°C Isothermal	10% SP.2250 mesh 100/120 Suplecoport by Supelco Glass

where C_s = concentration of sample species,

C_c = known concentration of calibrating species,

A_s = area from GC in sample,

A_c = area of calibrating species,

MW_c = molecular weight of calibrating species,

MW_s = molecular weight of sample species.

2.4 KSU Single Pulse Shock Tube (KSU-SPST)

2.4.1. Introduction

The shock tube is a device in which a plane shock wave is produced by the sudden bursting of a diaphragm that separates two pressure regions: region 1 with a gas at low pressure (from 0.25 to 0.66 atm) and region 4 with a gas at high pressure (around 19 atm). After bursting the diaphragm a compression wave is formed in the low pressure gas. This compression wave is accompanied by a sudden temperature and pressure pulse (regions 2, 3) which heats up the gaseous sample at the end of the low pressure region (test section). Simultaneously and in the opposite direction, an expansion or rarefaction wave moves into the high pressure gas at the speed of sound of this gas. The reflection of the shock at the end wall produces a further rise in temperature and pressure in the low pressure gas. However, the arrival of the reflected expansion wave into this region which will be denoted with the subscript 5, produces a fast and uniform decrease in temperature and pressure which will be explained later. See Fig. 3 for better understanding of this process. This whole process occurs in a few milliseconds and after each shock wave experiment is performed, all samples are collected to be analyzed by gas and liquid chromatography.

2.4.2 KSU-SPST Design and Operation

The Kansas State University shock tube was first built and tested by Seeker in 1976[35] [based on the original design by Glick in 1955]. After some modifications by Vaughn in his soot studies from benzene[2] other authors have performed studies using this shock tube on benzene and cyclohexane for soot formation.[36,37,38] For more information about shock tube design and theory, the reader should consult Gaydon and Hurle.[34]

The shock tube has been built using type 304 stainless steel with inside diameter 5.08 cm and wall thickness of 0.635 cm capable of withstanding a pressure of 205 atm. It is divided into two pressure regions: a high pressure region or driver section, and a low pressure region or experimental section where the test section is located (see Fig. 4).

The driver section is of variable length (2-3 m) to change the reaction time in the test section. This section has two pressure gauges to measure the initial driver pressure P_4, and the final pressure P_f after the shock wave is trapped in the dump tank ($\sim$ 3 atm). Helium was selected for driver gas because it is an inert gas and its low molecular weight permits the strongest shocks.

The experimental section includes the dump tank and the test section. In the test section the reactant mixture is injected by means of a gas line connected at the end wall (see Fig. 5). Two pressure transducers are located in this section 19.75 cm apart in order to record the time the shock wave travels this distance for computing other shock wave parameters (see discussion in next section). A ball valve

Fig. 3. Behavior of Shock Wave Parameters (Time, Pressure, and Temperature) After Bursting of Diaphragm.

a) Conventional Shock Tube

b) An (x-t) diagram showing progress of the shock wave, the rarefaction fan and the contact surface separating driver and experimental gases.

c) The pressure distribution along the tube at time t_1.

d) The temperature distribution at time t_1.

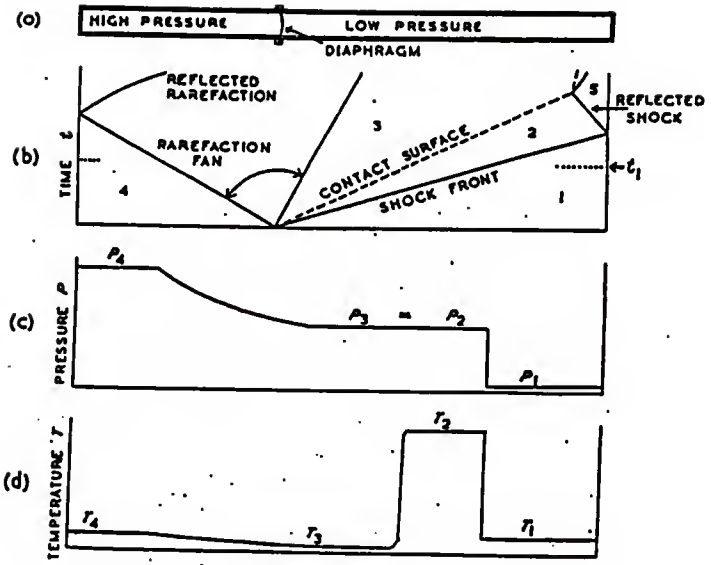
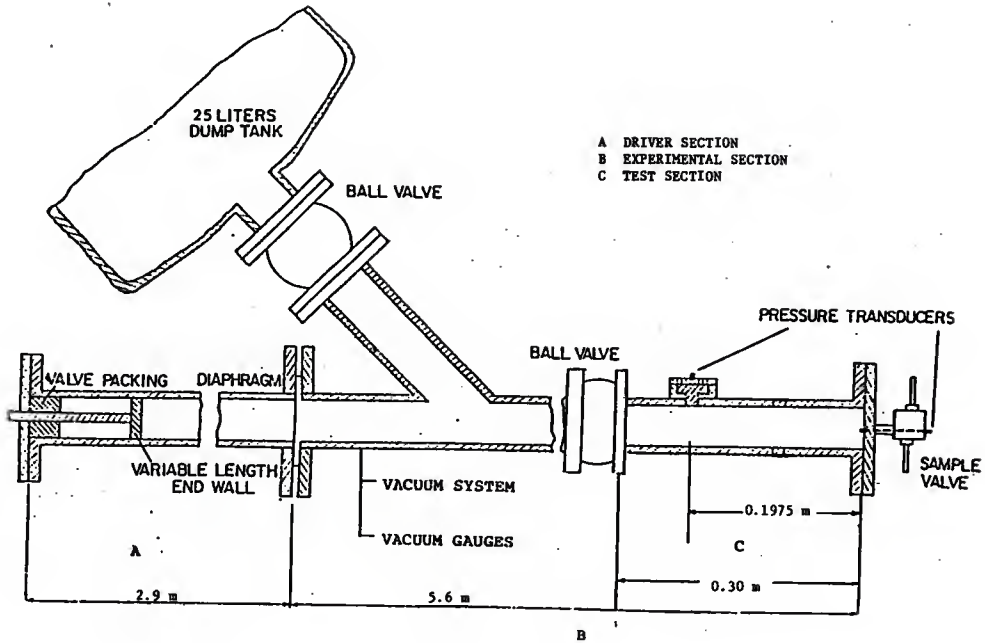

(a)
HIGH PRESSURE
LOW PRESSURE
DIAPHRAGM
(b)
TIME t
REFLECTED RAREFACTION
RAREFACTION FAN
CONTACT SURFACE
SHOCK FRONT
REFLECTED SHOCK
4
3
2
1
5
t_1
(c)
PRESSURE p
p_4
$p_3 = p_2$
p_1
(d)
TEMPERATURE T
T_4
T_3
T_2
T_1

Fig. 4. Shock Tube Diagram.

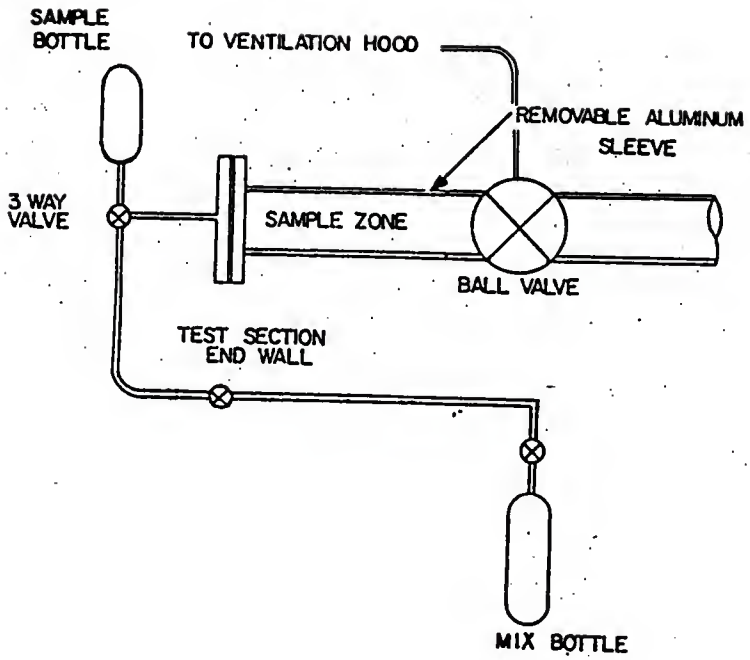

25 LITERS
DUMP TANK
BALL VALVE
A DRIVER SECTION
B EXPERIMENTAL SECTION
C TEST SECTION
PRESSURE TRANSDUCERS
BALL VALVE
VALVE PACKING
DIAPHRAGM
VARIABLE LENGTH
END WALL
VACUUM SYSTEM
VACUUM GAUGES
SAMPLE
VALVE
0.1975 m
A
C
2.9 m
5.6 m
0.30 m
B

separates this region from the rest of the shock tube. At the other end of the experimental section and near the diaphragm assembly there is a 40 liter dump tank connected in an obtuse angle to the shock tube which serves as the shock wave trap. The experimental or driven section is 5.9 m long and argon is used because it is an inert gas and has a constant specific heat ratio.

The mechanism for bursting the aluminum diaphragms (OCLAD 0.04 cm) was modified. Originally, the diaphragms were ruptured manually with a plunger located in an acute angle with the driver section near the diaphragm assembly. A new system described in detail in Appendix B was designed by the author in conjunction with Kent Sutton (conducting experiments on benzene pyrolysis). This new system allows a better reproduction of the experimental conditions. The system is electrically driven and performs by de-energizing an electro-magnet that holds the plunger in position by compressing a stainless steel spring. Once the magnet is turned off, the spring expands and drives the plunger into the diaphragm assembly and the shock wave is initiated.

Long before the experiment, a mixture bottle (stainless steel, 1 liter) is prepared with calculated amounts of toluene and argon (see Appendix A). The concentration of toluene is then checked by gas chromatography. This mixture is introduced into the previously evacuated test section. Pure argon at the same pressure is then injected into the rest of the experimental section (the test section is separated from the rest of the shock tube by closing ball valve). Once these two steps are performed the gauges (speedivac 0-760 torr) that measure the pressure in the experimental section are shut. At the same

Fig. 5. Close up of Test Section Showing the System for Gas Sampling.


SAMPLE BOTTLE
TO VENTILATION HOOD
REMOVABLE ALUMINUM SLEEVE
3 WAY VALVE
SAMPLE ZONE
BALL VALVE
TEST SECTION END WALL
MIX BOTTLE

time that the first steps are performed, the driver section is also evacuated. Then, the helium driver gas is introduced to a prescribed pressure and the shock wave is ready to be fired. The steps taken to start the shock wave are performed in a very short time; these are: swinging the ball valve in line, turning off the electro-magnet, and shutting the ball valve closed again. After a period of three hours, the samples are collected from the test section and analyzed by chromatography. A more detailed explanation of the shock-wave initiation procedure is presented in Appendix C.

2.4.3 Determination of Shock Wave Parameters

According to Gaydon and Hurle[34] when a compression wave is formed in the low pressure zone the speed of sound in argon is given by

$$a_1 = \sqrt{\gamma R T_1 / MW} \tag{2.2}$$

where γ is the specific heat ratio, R is the universal gas constant, T_1 is the temperature before the shock wave is fired and MW is the molecular weight of argon. For a temperature of T_1 = 298 K, a_1 is 321 m/sec. Then, the application of the conservation of mass, momentum, and energy equations when ideal behavior and constant specific heat are assumed, yields the following relations used to calculate the temperature and pressure at the reflected region 5 as

$$T_5 = T_1 \frac{[2(\gamma-1)M^2 + (3-\gamma)][(3\gamma-1)M^2 - 2(\gamma-1)]}{(\gamma+1)^2 M^2} \tag{2.3}$$

$$P_5 = P_1 \left\{\frac{2\gamma M^2 - (\gamma-1)}{\gamma+1}\right\} \left\{\frac{(3\gamma-1)M^2 - 2(\gamma-1)}{(\gamma-1)M^2 + 2}\right\} \tag{2.4}$$

and $M = u/a_1$ (2.4.1)

$u = d/t$ (2.4.2)

where M is the mach number of the incident shock wave, γ is the specific heat ratio of the gas, d is the distance between pressure transducers (19.75 cm), t is the time it takes for the shock wave to travel distance d, and T_1, P_1 are the temperature and pressure in region 1. The mach number is typically 2, and can be calculated from the recorded time 't' in the Fluke (model 1952B) time counter. The shock wave passes by the two pressure transducers installed 19.75 cm apart in the test section, and the elapsed time is recorded. This amplified voltage goes also into the Tektronix oscilloscope where a pressure history is recorded which will be useful in calculating the cooling rate addition to the reaction time (see Appendix D for detailed discussion).

2.4.4 Temperature Verification from Reflected Shock Study

Studies by previous authors using the KSU shock tube[2,35,36,37,38] have determined an increase in the shock wave temperature and pressure when reflection is allowed to occur at the end wall. A study for comparing the ideal temperature and pressure (Eq. (2.3) and (2.4)) with the actual values in the shock tube was performed due to the importance of these two parameters in the experiments.

A series of shock experiments were performed where the incident and reflected velocities were measured. The time 't_I' travelled for the incident shock was measured with the Fluke timer and the time 't_R' for the reflected shock was measured by using the oscilloscope. These two measured parameters 't_I' and 't_R' were necessary to compute the incident

and reflected mach numbers (M_I, M_R) by letting t_I or t_R = t in Eq. (2.4.2) and the Mach number M_R or M_I = M in Eq. (2.4.1) where d was kept constant at 19.75 cm. and these were used in the equation

$$\frac{T'}{T} = \frac{\left[\gamma M_1^2 - \frac{(\gamma-1)}{2}\right]\left[\frac{(\gamma-1)}{2} M_1^2 + 1\right]}{\left[\frac{\gamma+1}{2}\right]^2 M_1^2} \tag{2.5}$$

where M_1 = mach number M_I or M_R, and also in Eq. (2.3) for T_5.

For a temperature T_1 = 298 K, Eq. (2.5) was used to compute T_2 by letting $M_1 = M_I$, $T' = T_2$, and $T = T_1$. Then, the ratios between T_2/T_1 and T_5'/T_2 were set equal at the end wall as

$$\frac{T_2}{T_1} = \frac{T_5'}{T_2} \tag{2.6}$$

using Eq. (2.5) again for the ratio T_5'/T_2 where $M_1 = M_R(t_R)$, the reflected temperature T_5' was obtained. Collected data for this study is shown in Table 4 for long and short shock tube geometries using argon as the driven gas.

The calculated incident and reflected shock temperatures (T_5, T_5') were fitted using least squares methods to yield the following empirical relationships:

$$T_5' = (0.9134\ T_5 + 15.8320)K \quad r^2 = 0.9876 \tag{2.7}$$

$800 \leq T \leq 1250$ K

long geometry.

and

Table 4. Experimental Data for Temperature Calibration of the Short and Long Shock Tube Geometries

t_R (μsec)	t_I (μsec)	T_5' (K)	T_5 (K)
Short Tube Data			
500	264	1266	1348
502	262	1278	1367
517	274	1175	1257
499	264	1267	1348
536	282	1105	1192
529	280	1125	1208
497	260	1294	1380
493	256	1331	1421
532	284	1097	1176
499	271	1220	1286
294	265	1264	1335
507	274	1188	1257
479	264	1289	1341
492	266	1262	1329
493	269	1238	1298
Long Tube Data			
542	273	1157	1269
528	370	1192	1295
547	289	1058	1145
512	275	1178	1252
533	279	1129	1220
523	280	1135	1212
543	287	1073	1160
589	316	891	976
551	291	1043	1131
564	312	929	999
552	310	949	1010
541	298	1017	1084

$$T_5' = (0.9753\ T_5 - 45.4235)K \quad r^2 = 0.9829 \quad (2.8)$$

$$1250 \leq T \leq 1700\ K$$

short geometry.

Equation (2.3) overpredicts the temperature value by only 7% (70 K) in the temperature range 800-1250 K and by 5.5% (equivalent to 83 K) in the temperature range 1250-1700 K. Equations (2.7) and (2.8) were used in calculating the actual shock tube temperature from experimental data used in Eq. (2.3) to calculate T_5.

2.5 Post-Shock Sampling Systems

Once a shock wave was performed, the solid and gaseous samples were allowed to equilibrate for three hours. After this step, the samples were collected in two different ways depending on their nature (solid or gaseous).

2.5.1 Gaseous Collection

The gaseous collection is the simplest way of sampling, and it was performed by filling two 75 cm^3 stainless steel bottles which were previously evacuated to 1.32×10^{-6} atm., provided with a quick connection in one side and an injection port in the other side. The two bottles were connected to the end wall of the shock tube by means of a three-way valve (see Fig. 5). The first bottle (dump) was neglected for analysis and was used only as a storage for all impurities that were present in the sampling lines. These impurities came in the form of toluene and argon from the mixture bottle which was originally connected to the line where the dump bottle was also connected. Also, air could

have leaked into the lines when the mixture bottle was disconnected from the test section.

2.5.2 Solid Collection

The high molecular products (those with molecular weight greater than that of toluene) were collected in a cylindrical and removable aluminum liner located in the test section of the shock tube. After each experiment, the liner was immersed into a solvent (CS_2) for at least 8 hours. Then, the solvent containing the solid samples was distilled at 319 K; the volume of solution was reduced to 1 cm^3 and kept for further analysis in the Tracor GC analyzer. The liner was heated for 12 hours to evaporate residues of CS_2 and other impurities, before it was used again in a new experiment.

Standard samples for the Tracor chromatograph were prepared using bibenzyl, diphenyl methane and biphenyl in solution with carbon disulfide (10^{-7}, 10^{-8} and 10^{-9} mol/cm^3 respectively). Other compounds present in the samples were detected by comparing retention times with known standards.

3.0 RESULTS AND DISCUSSION

The pyrolysis of vapor phase toluene was studied in the temperature range 800 - 1700 K for two concentrations. A reaction time study was performed at 1283 K in order to measure the extent of toluene decomposition as a function of reaction time. The results from these experiments can be divided into three categories: 1) reaction time study, 2) effect of temperature on toluene decomposition, and 3) modeling of toluene decomposition.

3.1 Reaction Time Study

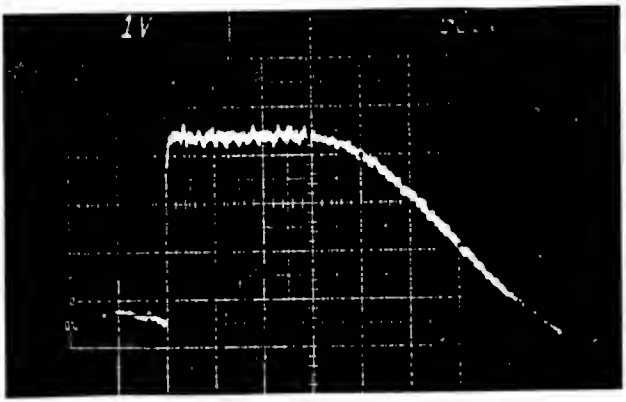
A series of shock tube experiments were performed where the length of the driver section in the shock tube was changed from 2 m to 3 m in order to change the reaction time.

As it was discussed in the previous chapter, when the diaphragm is burst a rarefaction fan is formed in the driver section. This rarefaction fan is reflected from the end wall of the driver section and when it arrives at the experimental section, the reaction is slowed down by decreasing the pressure and temperature in the test section. By changing the length of the driver section, the time of arrival of the cooling fan is also changed, and hence, the reaction time will also be changed. The oscilloscope trace (see Fig. 6) provides the shock pressure history where the flat portion represents the period of time when pressure and temperature P_5 and T_5 are constant (uncorrected reaction time). Then, the inclined section is where the pressure and the temperature decrease in an adiabatic process. The temperature can be calculated from the following equation,[2]

Fig. 6. Pressure History of the Shock Wave Recorded by the Tektronix Oscilloscope.

y-axis is pressure transducer response in volts.

x-axis is time.


1V

$$T(t) = T_5 \left[\frac{P(t)}{P_5}\right]^{(\gamma-1)/\gamma} , \qquad (3.1)$$

where

$$P(t) = P_5 - [dP/dt]t . \qquad (3.2)$$

The time derivative for the pressure dP/dt can be measured from the oscilloscope trace. γ is the specific heat ratio which for argon and helium is 5/3, 't' is the time it takes for the temperature to go from its highest value (T_5) to room temperature.

The conditions in these experiments were as follows

Temperature: 1283 ± 35 K
Average Toluene mol fraction in Argon: 6.7×10^{-3}
Reaction time: 0.8 - 3.0 msec

The concentration of the unreacted toluene was measured. The general form for the integrated expression for toluene disappearance can be written either as

$$\ell n \frac{[T]}{[T]_o} = -K_1 t \qquad n = 1 \qquad (3.3)$$

or

$$[T]^{1-n} - [T]_o^{1-n} = - K_n t(1-n) \qquad n \neq 1 \qquad (3.4)$$

where K is the reaction rate constant, [T] is the concentration of toluene at time 't' and $[T]_o$ is the initial concentration of toluene. Calculations were made of each condition by use of Eqs. (3.3) and (3.4) with assumed reaction orders of 1, 1.5, and 2. The results are shown in Table 5 where r^2 is the correlation coefficient for the least squares

fit. Least-squares regression analysis of the data resulting from plotting the left hand side of the equations (3.3) and (3.4) versus time 't' for each assumed order are shown in Tables 5 and 6, and it indicates that the best fit to the data is obtained when the reaction order of one is assumed. The correlation coefficient r^2 draws this conclusion where a value close to one indicates a better fit. The first order plot is shown in Fig. 7. These results are in good agreement with results initially reported by Swarc[39] and later by other authors.[13,17,19,20,22,31]

3.2 Effect of Temperature on Toluene Decomposition

A series of experiments were performed where the product yields were determined as a function of temperature for two initial mol fractions of toluene in argon: 7.4×10^{-3} and 1.25×10^{-2}. These concentrations were selected over higher values so that a constant specific heat ratio (γ) for the mixture could be assumed. A higher concentration would cause an undesirable specific heat ratio temperature dependence. The reaction (corrected) time was kept constant at 1.97 ± 0.13 msec for the temperature range 1100 - 1700 K, and also at 3.25 ± 0.24 msec for the range 800 - 1100 K.

A list of the observed products in these experiments is shown in Table 7. These compounds were detected by the chromatographic analysis comparing retention times with known samples, and their concentrations were determined by comparison with calibration standards.

Plots of the major percent product yields per millisecond of reaction versus reaction temperature is shown in Figs. 8(a) through (h).

Table 5. Least Squares Fit Results for Reaction Time Study.

Reaction Order	K (mole,K,sec)	r^2
1.0	418.1	0.8532
1.5	1.45×10^6	0.8162
2.0	5.01×10^9	0.7757

r^2 = correlation coefficient for Least Squares Fit.

K = Reaction Rate in mole,cm, sec units.

Fig. 7. Toluene Thermal Decomposition Curve That Verifies First Order Behavior. T = 1283 K, Initial Toluene Concentration = 0.67%

ln [CI]/[CI]o
1
.9
.8
.7
.6
.5
.4
.3
.2
.1
0
.9
1.1
1.3
1.5
1.7
1.9
2.1
2.3
REACTION TIME (msec)

Table 6. Experimental Data used for Least Squares Analysis in Reaction Time Study.

t (msec)	$-\ln[[T]/[T]_o]$	$2(1/[T]^{\frac{1}{2}} - 1/[T]_o^{\frac{1}{2}})$	$(1/[T] - 1/[T]_o)$
1.74	0.456	$1.40 * 10^3$	$4.28 * 10^6$
1.55	0.304	$8.74 * 10^2$	$2.53 * 10^6$
2.28	0.877	$3.07 * 10^3$	$1.08 * 10^7$
0.92	0.285	$9.17 * 10^2$	$2.99 * 10^6$
1.30	0.301	$9.77 * 10^2$	$3.19 * 10^6$
1.23	0.139	$4.27 * 10^2$	$1.39 * 10^6$
0.97	0.30	$8.70 * 10^1$	$2.51 * 10^5$

Table 7. Products from Toluene Decomposition Observed in this Study.

Methane	CH_4
Ethylene	C_2H_4
Acetylene	C_2H_2
Propadiene	C_3H_4
Propyne	C_3H_4
Propene	C_3H_6
Vinylacetylene	C_4H_4
Diacetylene	C_4H_2
1,3 Butadiene	C_4H_6
Styrene	C_8H_8
Benzene	C_6H_6
Biphenyl	$C_{12}H_{10}$
Diphenyl Methane	$C_{13}H_{12}$
Bibenzyl	$C_{14}H_{14}$

Also traces of C_9, C_{10}, C_{18} unidentified compounds.

These major product yields are acetylene, benzene, methane, and ethylene, and their percent yield is calculated by dividing the composition of the product by the initial composition of toluene injected into the test section. The yields of minor products (C_3, C_4, and high molecular weight hydrocarbons) are presented in Appendix H. The major conclusion from these plots is that benzene is the major product formed at low temperatures reaching a maximum yield at 1425 K. This is the first time that benzene has been observed with this high yield in shock tube low temperature, thermal decomposition of toluene. R. Smith[25,26,40] observed benzene and other hydrocarbons using a Knudsen cell and the following experimental conditions:

Temperature Range:	1173 - 2073 K
Reaction Pressures:	9.87×10^{-9} - 9.87×10^{-5} atm.
Reaction Time:	3×10^{-3} $(M/T)^{\frac{1}{2}}$ sec
	M = molecular weight
	T = temperature
Range:	0.840 - 0.632 msec

In this study, higher reaction pressures were used in excess of 10 atm the reaction time was maintained at around 2 msec for shock waves with temperatures above 1100 K and at around 3.25 msec at lower temperatures. It is important to note that the low weight product yields in Smith's work are very similar to the ones found in this work (see Table 8) with the only difference in the yield vs. temperature distribution, where the maximum yield of most species occurs at 1673 K which is 248 K higher than the temperature where most of the species observed in this study reach their highest yield (1425 K). However, acetylene is first observed at 1273 K by Smith which is close to the threshold temperature for the production of such species in this study (1300 K).

Fig. 8. Product Yield vs. Temperature Distribution for Major Products in Toluene Pyrolysis.

(a) Acetylene, Initial Toluene Mol Concentration (ITC) = 1.25%

(b) Acetylen, ITMF = 0.74%

(c) Benzene, ITMF = 1.25%

(d) Benzene, ITMF = 0.74%

(e) Methane, ITMF = 1.25%

(f) Methane, ITMF = 0.74%

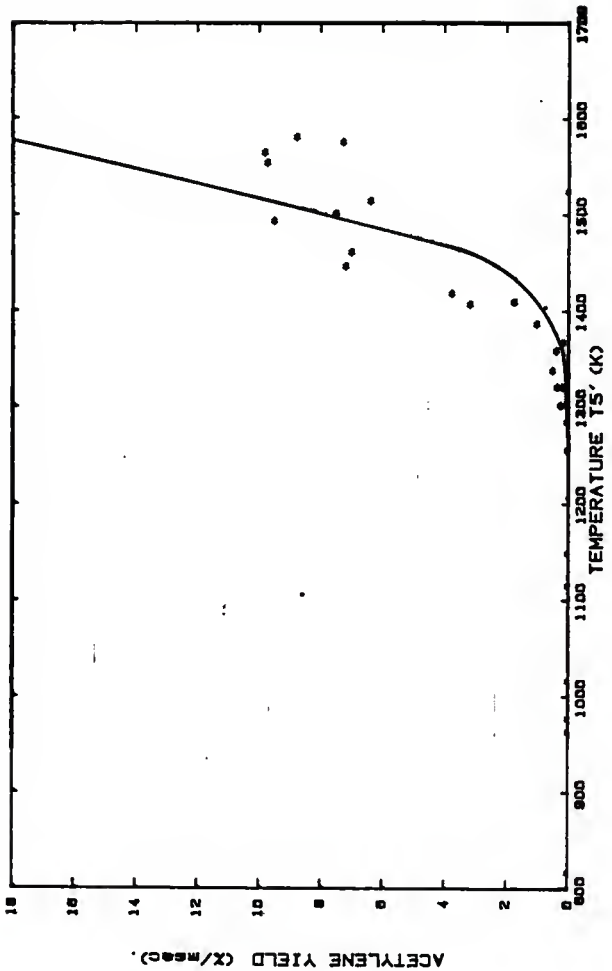
(g) Ethylene, ITMF = 1.25%

(h) Ethylene, ITMF = 0.74%

(i) Toluene, ITMF = 1.25%

(j) Toluene, ITMF = 0.74%

Note: solid lines represent computer model results.


ACETYLENE YIELD (%/mseo).
TEMPERATURE 'TS' (K)
0
2
4
6
8
10
12
14
16
18
800
900
1000
1100
1200
1300
1400
1500
1600
1700

(a)

ACETYLENE YIELD (%/msec).
TEMPERATURE T5' (K)
0
2
4
6
8
10
12
14
16
18
800
900
1000
1100
1200
1300
1400
1500
1600
1700

(b)

BENZENE YIELD (%/msec).
TEMPERATURE T5' (K)
0
.5
1
1.5
2
2.5
3
4
4.5
5
5.5
6
800
900
1000
1100
1200
1300
1400
1500
1600
1700

(c) 54

BENZENE YIELD (%/msec)
0
.5
1
1.5
2
2.5
3
3.5
4
4.5
5
5.5
6
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE T5' (K)

(d)

METHANE YIELD (%/mseC)
4
3.5
3
2.5
2
1.5
1
.5
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE TS' (K)

(e)

METHANE YIELD (%/msec)
4
3.5
3
2.5
2
1.5
1
.5
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE T5' (K)

(f)

ETHYLENE YIELD (%/msec).
1.2
1
.8
.6
.4
.2
0
600
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE TS' (K)

(g)

ETHYLENE YIELD (%/msec)
1.2
1
.8
.6
.4
.2
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE TS' (K)

(h)

(f)

(f)

Table 8. Product Yield[(a)]-Temperature Distribution Results from R. Smith Studies[25]

Species	Temperature (K) 1173	1273	1373	1473	1573	1673	1773	1873	2073
CH_3		0.31	1.5	11.0	24.0	15.0	5.2	2.1	0.26
CH_4			0.44	2.0	4.9	4.9	5.0	3.8	0.4
C_2H_2		0.02	0.09	2.0	16.0	37.0	65.0	78.0	80.0
C_2H_3				0.14	0.78	1.7	3.0	4.0	4.5
C_2H_4			0.12	0.09	0.20	5.2	3.2	2.5	1.5
C_3H_3		∿0.01	0.09	1.3	5.0	5.4	1.2	0.4	0.2
C_3H_4				0.19	0.78	0.8	0.3	0.3	0.5
C_3H_5			0.06	0.21	0.25	0.1			
C_4H_2		∿0.01	0.01	0.68	4.1	6.3	5.5	5.0	12.0
C_4H_3			0.03	0.20	0.4	0.7	0.4	0.3	0.
C_4H_4			0.03	0.20	0.8	1.2	0.7	0.3	
C_5H_3			0.02	0.33	0.8	0.7	0.1		
C_5H_4			0.01	1.10	0.3	0.2	0.01		
C_5H_5		0.18	1.2	3.5	2.8	1.0	0.1		
C_5H_6		0.08	0.13	0.31	0.3	0.1			
C_6H_2				0.01	0.2	0.6	0.35	0.3	0.3
C_6H_4				0.24	0.7	0.8	0.36	0.1	
C_6H_5		0.06	0.15	0.64	1.1	1.3	0.7	0.25	
C_6H_6		0.13	0.90	4.4	10.0	11.0	7.0	3.0	0.5
C_7H_5		0.03	0.17	1.2	1.7	0.6	0.05		
C_7H_6				1.0	1.0	0.3	0.01		
C_7H_7	14.0	30.0	40.0	37.0	16.0	2.5	0.1	0.02	
C_7H_8	86.0	69.0	56.0	33.0	8.4	1.1			
C_8H_2						0.03	0.01		
C_8H_6				0.07	0.45	0.6	0.2	0.4	
C_8H_8				0.10	0.33	0.15			
C_9H_7				0.08	0.5	0.4	0.06		
$C_{10}H_6$				0.01	0.07	0.08	0.03		
$C_{10}H_8$				0.02	0.2	0.4	0.15	0.01	
$C_{11}H_7$				0.01	0.09	0.06			
$C_{12}H_8$				0.03	0.18	0.2	0.05	0.01	
$C_{12}H_9$				0.20	0.6	0.17	0.01		
$C_{14}H_{10}$				0.03	0.09	0.07	0.01		

(a) Mole percent excluding hydrogen and H_2. Knudsen cell with 2 mm orifice.

The yield of methane as a function of temperature is shown in Figs. 8(e) and (f), and it reaches a maximum value at 1500 K. Methane first appears at 1300 K which is somewhat higher than the temperature at which benzene begins to appear. Smith observed methane reaching its highest yield at 1773 K and appearing first at 1373 K. Ethylene first appears at a lower temperature (1250 K) and reaches a maximum at 1425 K. The yields of ethylene as a function of temperature are shown in Fig. 8(g) and (h).

Acetylene is observed at 1300 K and increases rapidly above 1425K when the yield of benzene and ethylene start decreasing. This is shown in Figs. 8(a) and (b). This rapid increase in the yield of acetylene as a function of temperature coupled with the rapid decrease in toluene concentration and the yield of benzene suggests that fragmentation of the tolyl radical becomes more important with increasing temperature.

The yields of the high molecular weight products, biphenyl ($C_{12}H_{10}$), diphenylmethane ($C_{13}H_{12}$) and bibenzyl ($C_{14}H_{14}$) are orders of magnitude smaller than the yields of benzene and these are shown in Appendix H. These results indicate that the cleavage of the methyl group from toluene,

$$C_6H_5\text{-}CH_3 \longrightarrow C_6H_5^{\bullet} + CH_3^{\bullet} \qquad (3.5)$$

does not compete with the C-H bond cleavage

$$C_6H_5\text{-}CH_3 \longrightarrow C_6H_5CH_2^{\bullet} + H^{\bullet} \ . \qquad (3.6)$$

A series of experiments were performed in which the toluene mol fraction in the bath was maintained constant at about 0.74 x 0.002%

and the corrected reaction time was kept at 2.01 ± 0.21 msec. The temperature was varied from 1100 to 1700 K. The resultant major product yield curves are shown in Figs. 8(b),(d),(f),(h) and the other product yield curves can be found in Appendix H. By comparing the curves from the previous experiment with the new ones, a similar product. temperature profile is observed which means that the decomposition of toluene is of first order. This is because when the original initial toluene mol fraction of 1.25×10^{-2} was decreased by half, (to around 7.4×10^{-3}), the product yields also decreased by half. Also, the toluene decomposition curve is very similar to the one from 1.25×10^{-2} toluene mol fraction in argon (see Fig. 8(i),(j)).

3.3 Modeling of Toluene Decomposition

The present section will discuss the reaction mechanisms involved in the thermal decomposition of toluene. First, a small review of the literature describing some of the proposed mechanisms in toluene pyrolysis. Then, an explanation of the modeling techniques used to describe the experimental data from the present work.

3.3.1 Proposed Reaction Mechanisms

A review of the literature shows an agreement among the toluene pyrolysis experimentalists in the first steps involved in toluene decomposition. No matter how the pyrolysis is performed (flow system, static system or shock tube) or what the conditions of concentration, pressure and temperature are, the first three proposed reactions are

$$C_7H_8 \longrightarrow C_7H_7\cdot + H\cdot \qquad (3.5)$$

$$H\cdot + C_7H_8 \longrightarrow C_7H_7\cdot + H_2\cdot \qquad (3.6)$$

$$H\cdot + C_7H_8 \longrightarrow C_6H_6 + CH_3\cdot \qquad (3.7)$$

In 1947, M. Swarc[39] was the first experimentalist to propose a reaction mechanism. Working with a flow reactor he observed hydrogen, methane and bibenzyl as the relevant products. Based on these observations he proposed a mechanism that included Eqs. (3.5), (3.6), (3.7) and also the following for bibenzyl formation

$$CH_3\cdot + C_7H_8 \longrightarrow C_7H_7\cdot + CH_4 \ , \qquad (3.8)$$

$$2\ C_7H_7\cdot \longrightarrow C_{14}H_{14}\ \text{(bibenzyl)} \ . \qquad (3.9)$$

He also reported a reaction rate constant for reaction (3.5) given by

$$K_1 = 2.1 \times 10^{13} \exp(-324.5\ (kJ)/RT)\ sec^{-1}$$

Following the work performed by Swarc, Steacie, et al.[27] in 1954 argued about the possibility of the reaction

$$C_7H_8 \longrightarrow C_6H_5\cdot + CH_3\cdot \qquad (3.10)$$

to explain the formation of methane, based on the fact that they found a higher activation energy for reaction (3.5) (376.8 kJ) than the value reported by Swarc.

Later, M. Takahasi[18,41] in 1959 and S. J. Price[19] in 1961 working with flow systems, proposed a new set of reactions. Takahasi explained the formation of hydrogen and methane by hydrogen atom and methyl radical abstraction

$$C_7H_8 + H\cdot \longrightarrow C_7H_7\cdot + H_2 \ , \qquad (3.6)$$

and

$$C_7H_8 + CH_3\cdot \longrightarrow C_7H_7 + CH_4 \quad . \qquad (3.11)$$

Price also included reactions (3.6) and (3.11) into the mechanism and added the reaction

$$2\ CH_3\cdot \longrightarrow C_2H_6 \quad , \qquad (3.12)$$

to explain the formation of ethane

In 1971, Peacock et al.,[20] introduced two new reactions to the mechanism

$$CH_3\cdot + H_2 \longrightarrow CH_4 + H\cdot \qquad (3.13)$$

$$C_7H_7\cdot + H_2 \longrightarrow C_7H_8 + H\cdot \qquad (3.14)$$

Reaction (3.13) produces more hydrogen atoms which are used by reaction (3.7) to form benzene and reduces the formation of bibenzyl via reaction (3.8) and (3.9). R. Smith using Knudsen Cells (in 1979) argued that acetylene was the main precursor for soot formation based on his acetylene yields from toluene pyrolysis. He proposed the reactions:

$$C_7H_7\cdot \longrightarrow C_5H_5\cdot + C_2H_2 \qquad (3.15.a)$$

$$C_7H_7\cdot \longrightarrow C_4H_4 + C_3H_3\cdot \qquad (3.15.b)$$

$$C_5H_5\cdot \longrightarrow C_5H_3\cdot + H_2 \qquad (3.16)$$

$$C_4H_4 \longrightarrow C_4H_2 + H_2 \qquad (3.17)$$

$$C_4H_4 \longrightarrow C_4H_3 + H\cdot$$

where other compounds like vinylacetylene and diacetylene also played an important role in soot formation. A summary of the initial reactions in toluene pyrolysis proposed by these authors is shown in Table 9.

3.3.2 Modeling of Experimental Data

The process of modeling the experimental product yields is a very simple one. First, all the possible reactions (Fig. 9) and other reactions that involve benzene decomposition were included in the pyrolysis mechanism. Reaction rate constant values were provided by the literature. A system of first order differential equations was set up of the form

$$\frac{d[A]}{dt} = K_i[A][C[+ K_j[B][A] + K_k[C][B]$$

$$\frac{d[B]}{dt} = K_k[B][A] + K_j[C][A] + K_i[B][A]$$

etc.

where [A], [B], [C], etc, are the concentration of each species present in the system, K values are the rate constant for reactions i, j, k, etc., and dt is the time derivative. The literature values for the rate constants are shown in Fig. 9.

The system of equations was solved for each temperature value from 1100 K to 1700 K by using a computer program which is described in Appendix F. This computer program was partially provided by the I.M.S. Library routine DGEAR written in Fortran (double precision). The method of solution for this system of equations is basically the backward differentiation formula also called Gear's stiff method. The computer programming system was used in the following way. First of all, a system of first order differential equations was set up including the

Table 9. Chemical Reaction Proposed by the Literature in Toluene Pyrolysis

$C_7H_8 \longrightarrow C_7H_7\cdot + H\cdot$
$H\cdot + C_7H_8 \longrightarrow C_7H_7\cdot + H\cdot$
$H\cdot + C_7H_8 \longrightarrow C_6H_6 + CH_3\cdot$
$CH_3\cdot + C_7H_8 \longrightarrow C_7H_7\cdot + CH_4$
$2\ C_7H_7\cdot \longrightarrow C_{14}H_{14}$
$C_7H_8 \longrightarrow C_6H_5 + CH_3\cdot$
$C_7H_8 + H\cdot \longrightarrow C_7H_7\cdot + H_2$
$C_7H_8 + CH_3\cdot \longrightarrow C_7H_7\cdot + CH_4$
$2\ CH_3\cdot \longrightarrow C_2H_6$
$CH_3\cdot + H_2 \longrightarrow CH_4 + H\cdot$
$C_7H_7\cdot + H_2 \longrightarrow C_7H_8 + H\cdot$
$2\ C_7H_7 \longrightarrow C_5H_5 + C_2H_2$
$C_5H_5 \longrightarrow C_5H_3\cdot + H_2$
$2\ C_4H_4 \longrightarrow C_4H_2 + H_2 + C_4H_3 + H\cdot$

Fig. 9. Reported Reactions in Toluene Pyrolysis and their Respective Reaction Rate Constants used Initially in Computer Modeling. Units: mole, sec, k, cm^3.

References:
1) Skinner and Subba Rao[23]
2) Empirical Value
3) Astholz, Durant and Troe[31]
4) Kern, Skinner, et. al.[30]
5) Peacock, et. al.[20]
6) Asaba & Fujii[44]

$C_7H_8 \longrightarrow C_7H_7\cdot + H\cdot$	$K = 2.7\times10^{4} \exp(-347.5(kJ)/RT)$ [1]
$H\cdot + C_7H_8 \longrightarrow C_6H_6 + CH_3\cdot$	$K = 2.8\times10^{13} \exp(-15.5(kJ)/RT)$ [1]
$H\cdot + C_7H_8 \longrightarrow C_7H_7\cdot + H_2$	$K = 7.6\times10^{-5}T^{5.5} \exp(-1424(J)/RT)$ [1]
$2\ C_7H_7\cdot \longrightarrow C_5H_5\cdot + C_2H_2 + C_4H_4 + C_3H_3\cdot$	$K = 8.3\times10^{17} \exp(-455(kJ)/RT)$ [3]
$H\cdot + C_6H_6 \longrightarrow C_6H_5\cdot + H_2$	$K = 10^{1345} \exp(-67(kJ)/RT)$ [4]
$C_6H_6 \longrightarrow C_4H_4 + C_2H_2$	$K = 10^{14.11} \exp(-368(KF)/RT)$ [4]
$C_6H_6 \longrightarrow C_6H_5\cdot + H\cdot$	$K = 10^{15.08} \exp(-343(kJ)/RT)$ [4]
$C_6H_5\cdot \longrightarrow C_4H_3\cdot + C_2H_2$	$K = 10^{11.3} \exp(-214(kJ)/RT)$ [4]
$C_4H_3\cdot \longrightarrow C_4H_2 + H\cdot$	$K = 2.82\times10^{12} \exp(-59(kJ)/RT)$ [5]
$C_7H_7\cdot + H_2 \longrightarrow C_7H_8 + H\cdot$	$K = 10^{7.85} \exp(-42(kJ)/RT)$ [6]
$C_6H_6 + C_6H_5\cdot \longrightarrow C_{12}H_{10} + H\cdot$	$K = 10^{9.9} \exp(-72(kJ)/RT)$ [6]
$CH_3\cdot + C_6H_6 \longrightarrow C_7H_8 + H\cdot$	$K = 10^{9.5} \exp(-87(kJ)/RT)$ [6]
$CH_4 + C_6H_5\cdot \longrightarrow C_7H_8 + H\cdot$	$K = 10^{7.2} \exp(-39(kJ)/RT)$ [6]
$CH_3\cdot + C_6H_6 \longrightarrow CH_4 + C_6H_5\cdot$	$K = 10^{11.1} \exp(-224(kJ)/RT)$ [5]
$C_7H_8 + H_2 \longrightarrow C_6H_6 + CH_4$	$K = 10^{8.9} \exp(-46(kJ)/RT)$ [6]
$CH_4 + C_6H_5\cdot \longrightarrow CH_3\cdot + C_6H_6$	$K = 10^{9.6} \exp(-34(kJ)/RT)$ [6]
$C_6H_5\cdot + H_2 \longrightarrow C_6H_6 + H\cdot$	$K = 10^{11.5} \exp(-29(kJ)/RT)$ [6]
$C_{12}H_{10} + H\cdot \longrightarrow C_6H_6 + C_6H_5\cdot$	$K = 10^{11.5} \exp(-29(KJ)/RT)$ [6]
$C_6H_5\cdot \longrightarrow C_2H_2 + C_4H_2 + H\cdot$	$K = 1.2\times10^{15} \exp(-343(KJ)/RT)$ [1]
$CH_3\cdot + C_7H_8 \longrightarrow C_7H_7\cdot + CH_4$	$K = 10^{10} \exp(-15(KJ)/RT)$ [2]

stable and radical species shown in Fig. 10(1). For each species, the differential equation represented the rate of production and dissappearance of such species observed in the reaction mechanism first proposed (Fig. 9). Once the system of equations was set up for each species, literature values for the reaction rate constants were input in the program. Also, other parameters such as initial toluene concentration, reaction time, stepsize, and accuracy were input. A value of 2.87×10^{-7} mol/cm^3 for toluene concentration was selected because it was basically the value used in the experimental data (equivalent to 1.25×10^{-2} toluene mol fraction). A value of 2 msec was used for reaction time in a temperature range from 1100 K to 1700 K; however, the product yields were recorded for 1 msec of reaction time because the experimental data was normalized to 1 msec except for toluene which was observed at 2 msec. Since the reaction rate constant values were temperature dependent, the system of differential equations had to be solved for each input temperature value.

A sensitivity analysis was performed with the initial set of equations found in the literature (Fig. 10). The results from this analysis generated nine reactions (Fig. 11) which describe the temperature profiles for benzene, methane, and acetylene as well as the toluene decomposition in the temperature range 1100-1700 K. Figures 8(a),(c),(e)show the comparison between the experimental results and the expected yields from the model where the solid line represents the computer values. From these figures it is observed an almost perfect fit for benzene and acetylene yields, and a rather close fit for the

Fig. 10. Species used for Sensitivity Analysis

(1) Species used initially

(2) Species used in final model

Stable Species	
(1)	(2)
C_7H_8	C_7H_8
C_6H_6	C_6H_6
H_2	H_2
C_2H_2	C_2H_2
C_4H_4	C_4H_4
C_4H_2	CH_4
$C_{12}H_{10}$	
CH_4	
Radicals	
$C_7H_7\cdot$	$C_7H_7\cdot$
$H\cdot$	$H\cdot$
$CH_3\cdot$	$CH_3\cdot$
$C_5H_5\cdot$	$C_5H_5\cdot$
$C_3H_3\cdot$	$C_3H_3\cdot$
$C_6H_5\cdot$	$C_6H_5\cdot$
$C_4H_3\cdot$	$C_4H_3\cdot$

Fig. 11. Final Reactions Used for Computer Modeling of Experimental Data. Units: mole, K, sec, cm^3.

$C_7H_8 \xrightarrow{K_1} C_7H_7^+ + H\cdot$	$K_1 = 2.7\times10^{14} \exp(-307(kJ)/(RT)$
$H\cdot + C_7H_8 \xrightarrow{K_2} C_6H_6 + CH_3\cdot$	$K_2 = 0.4\times10^{13} \exp(-15(kJ)/RT)$
$H\cdot + C_7H_8 \xrightarrow{K_3} C_7H_7\cdot + H_2$	$K_3 = 7.6\times10^{-5}T^{5.5} \exp(-1424(J)/RT)$
$2\ C_7H_7\cdot \xrightarrow{K_4} C_5H_5\cdot + C_2H_2 + C_4H_4 + C_3H_3\cdot$	$K_4 = 8.3\times10^{17} \exp(-455(kJ)/RT)$
$H\cdot + C_6H_6 \xrightarrow{K_5} C_6H_5\cdot + H_2$	$K_5 = 10^{13.45} \exp(-67(kJ)/RT)$
$C_6H_6 \xrightarrow{K_6} C_4H_4 + C_2H_2$	$K_6 = 10^{14.11} \exp(-318(kJ)/RT)$
$C_6H_5\cdot \xrightarrow{K_7} C_4H_3\cdot + C_2H_2$	$K_7 = 10^{15.08} \exp(-343(kJ)/RT)$
$C_7H_7\cdot + H_2 \xrightarrow{K_8} C_7H_8 + H\cdot$	$K_8 = 2.82\times10^{12} \exp(-59(kJ)/RT)$
$CH_3\cdot + C_7H_8 \xrightarrow{K_9} C_7H_7\cdot + CH_4$	[a] $K_9 = 10^{13} \exp(-67(kJ)/RT)$

[a] Value generated by sensitivity analysis.

methane yields. This last discrepancy is due to the possible existence of other reactions which were not included in the reaction mechanism, and also to the experimental errors associated with each preexponential term and energy of activation in the reaction rate constants reported in the literature.

It is important to note that the originally reported values for the energy of activation in reaction (1) (Fig. 11) (347.5 kJ)[19] was changed by the sensitivity analysis to 307,326 J and 318,212 J. It is also important to note that different values have been reported for this crucial reaction. For example, Swarc[39] reported a value of 324.5 kJ, Takahasi[18,41] a value of 308.6 kJ in the temperature range 1011-1122 K, and Steacie, et al.[17] reported a value of 376.8 kJ. Also, the preexponential term in reaction (2) was changed from 0.4×10^{13} to 2.8×10^{13}; and the reaction rate constant of reaction (9) was generated by the analysis. This last value is an empirical result used to fit the experimental data and should not be interpreted as a calculated or measured reaction rate value. The validity of these changes is supported by the fact that the literature values were obtained in different experimental conditions to those in the present work.

3.4 Summary of Results

The reaction time study in shock tube pyrolysis of vapor phase toluene led to the conclusion that the reaction mechanism is of first order. This conclusion is also supported by the concentration studies where the toluene decomposition and product yield results at two

different initial toluene mol fraction in argon (1.25×10^{-2} and 7.4×10^{-3}) show that as initial concentration is increased by a factor of two, the product yields are also increased the same factor.

Product yields identified by gas and liquid chromatography were methane, ethylene, acetylene, propadiene, propyne, propene, vinylacetylene, diacetylene, 1-3 butadiene, benzene, and high molecular weight compounds such as bibenzyl biphenyl, diphenyl methane, styrene, and hypothesized traces of C_8, C_9, C_{10}, C_{18} compounds.

The observation of benzene high yields at low temperature shock tube study is of special importance because it is the first time that has been observed in such conditions and initially hypothesized reaction mechanisms for bibenzyl, biphenyl and diphenyl methane formation seem to play a smaller role in toluene pyrolysis. Modeling of benzene, methane and acetylene yields show a very good agreement between experimental results and theory.

The overall disappearance rate of reaction was calculated to be $K = 2.5 \times 10^{6} \exp(-107\ (kJ)/RT)\ sec^{-1}$ for the temperature range 1100-1700 K.

4.0 CONCLUSIONS AND RECOMMENDATIONS FOR FURTHER STUDY

The pyrolysis of vapor phase toluene was performed in the Kansas State University Single Pulse Shock Tube for three sets of conditions: 1) reaction time study, 2) effects of temperature studies, and 3) effects of concentration studies.

For the reaction time study, where the temperature and initial toluene mol fraction in argon were kept constant at 1283 ± 35 K and 6.7×10^{-3} respectively, and the reaction time was varied from 0.8 to 3.0 msec, the order of the reaction for toluene decomposition was determined to be first.

Also, concentration studies showed that the pyrolysis of toluene is of first order or autocatalytic. This conclusion has been drawn after increasing the initial toluene mol fraction in argon from 7.4×10^{-3} to 1.25×10^{-2} at a constant reaction time of 2.01 ± 0.21 msec in the temperature range 1100 - 1700 K. The results showed an increase by a factor of 2 of all the species yields after the initial toluene mol fraction in argon was doubled from 7.4×10^{-3} to 1.25×10^{-2}, that is explained by the first order reaction conclusion.

The main product yields from toluene pyrolysis were acetylene, benzene, methane, and ethylene. Minor products were propyne, propene, propadiene, diacetylene, vinylacetylene, styrene, bibenzyl, biphenyl and diphenyl methane. The yield of the first four compounds is of great importance because the initial hypothesis that motivated the present work to explain the formation of intermediate species to yield soot was convincingly rejected. This hypothesis included the reactions

$$C_7H_8 \longrightarrow C_7H_7 + H\cdot \quad (4.1)$$

$$C_7H_8 \longrightarrow C_6H_5\cdot + CH_3\cdot \quad (4.2)$$

leading to the formation of bibenzyl, biphenyl and diphenyl methane.

The production of benzene and methane in large amounts suggests that the toluene pyrolysis at these conditions follows a different reaction pattern which is

$$C_7H_8 \longrightarrow C_7H_7 + H\cdot \quad (4.3)$$

$$H\cdot + C_7H_8 \longrightarrow C_6H_6 + CH_3\cdot \quad (4.4)$$

$$CH_3\cdot + C_7H_8 \longrightarrow C_7H_7\cdot + CH_4 \quad (4.5)$$

Also, the increasing production of acetylene with increasing temperature which starts when all the other species begin to decline in production yield, suggests that the fragmentation process becomes predominant at around 1400 K.[42,11]

The use of computer programs for toluene decomposition produced a reaction mechanism which gives an estimate of the acetylene, benzene and methane yields as well as the toluene decomposition with a very good accuracy.

A few recommendations for further studies in toluene pyrolysis include the addition of some more sophisticated analytical devices to measure the behavior of free radicals as well as the use of isotopically labelled toluene to observe the production pattern of certain radicals which are important in the proposal of reaction mechanisms. Also, a qualitative and quantitative analysis should be performed on high molecular products to observe their behavior and role in the formation of soot at higher temperatures. Finally, mixture studies should be

performed where other compounds could be added to toluene and then pyrolyzed in order to observe the suppression of acetylene yield, and hence the suppression of soot.

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Appendix A - Gaseous Mixture Preparation

The preparation of the Toluene/Argon mixture to be used in the test section of the shock tube was performed in the following way. A one liter stainless steel bottle was equipped with an injection port and a quick connector. The bottle was evacuated and liquid toluene was injected. The amount of toluene and argon to be injected was determined from the ideal gas law

$$PV = nRT \tag{A.1}$$

where P is pressure, V is the volume, n is the number of moles, T is temperature and R is the universal gas constant. In Eq. (A.1) P can be written as

$$P_B = P(\text{toluene}) + P(\text{argon}) \tag{A.2}$$

where

$$P(\text{Toluene}) = \chi \cdot P_B \tag{A.3}$$

χ is the mol fraction of toluene in argon in the mixture bottle which in this study was changed from 1.25×10^{-2} to 7.4×10^{-3}. The vapor pressure of toluene at room temperature was calculated to determine the total pressure in the mixture bottle. The temperature dependence of the toluene vapor pressure is reported by Hancock[3] as

$$\log[P(\text{mmHG})] = 6.95508 - \left\{\frac{1345.087}{219.516 + T(°C)}\right\} \tag{A.4}$$

At an average room temperature of 25°C the vapor pressure of toluene is approximately 28 mmHg. Thus, using this value for P(toluene) in Eq. (A.3) the bottle total pressure was easy to determine for a

prescribed initial toluene mol fraction. The volume amount of toluene (V_T) injected was then determined from Eq. (A.1) as

$$V_T = \frac{P(\text{toluene})\ V(\text{bottle})\ MW(\text{toluene})}{R\ T\ \rho(\text{toluene})} \qquad (A.5)$$

where MW is the molecular weight.

The conditions applied in the present study were

Toluene mol fraction	Toluene Volume (cm^3)	Argon Pressure (atm)
0.0125	0.163	3.69
0.0074	0.098	3.04

Appendix B - Design of the New Electromagnetically Driven Plunger

The KSU Single Pulse Shock Tube was provided with a new feature which allowed a better reproduction of the shock wave temperature. This new feature was the electromagnetically driven plunger which burst the aluminum diaphragm. A picture of the new device is shown in Fig. B.1, where two stainless steel springs can be seen and the operating mechanism is similar to that of a pinball machine. Spring A is capable of compressing when the flat end of the plunger is held by the electromagnet; when this magnet is de-energized, the plunger is released with a force of about 445 N towards the diaphragm assembly in the shock tube, rupturing the aluminum, and initiating the shock wave. Spring B is used to stop the plunger so that it produces an even rupture in the diaphragm, and hence, a good shock structure.

This new device was tested for a number of shocks run at a pressure P_1 of 0.47 atm and P_4 = 19 atm using helium and argon as the driver and driven gases respectively. Table B.1 shows the experimental data for this test, where the average temperature was 1388 K with a deviation of ± 37 K or 2.3%. This result is much better than shocks run with the original manually driven plunger where temperature replications had a deviation range of about ± 10 to ± 15%.

The deviation observed using this new device was mostly attributed to the presumed difference in cold working the material when it was manufactured. For this reason, the aluminum diaphragms were annealed at 623 K for two days before they were used. It was also established that for even better replication of shock waves, small amounts of aluminum

diaphragms should be annealed because when they are used 2 or 3 days after annealing larger deviations in temperature occur.

Fig. B.1. New Electromagnetically Driven Plunger in the KSU Shock Tube.

(A) Driving Spring

(B) Stopping Spring

Table B.1. Experimental Data for Testing New Plunger.

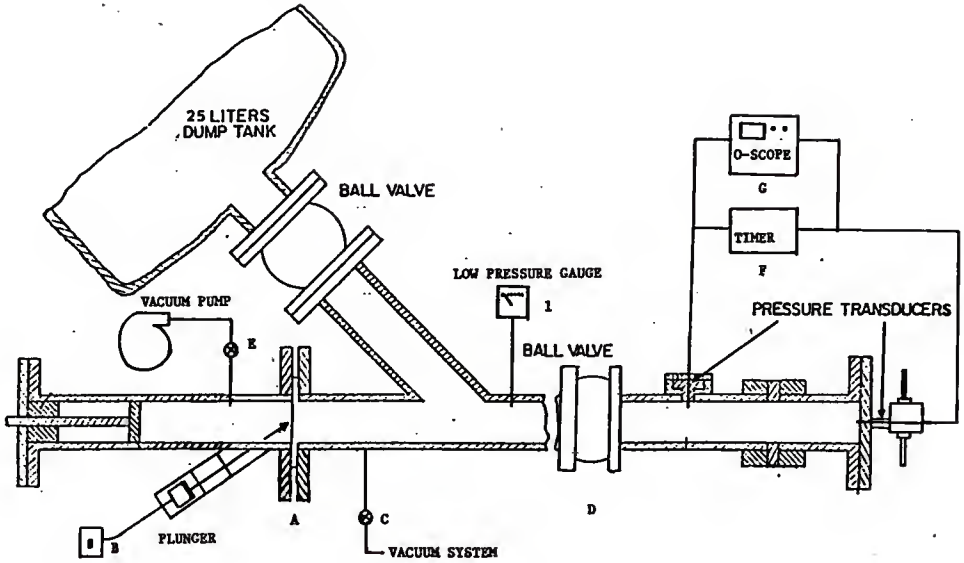
Run	Δt (msec)	T_5' (K)
1	0.2609	1378
2	0.2598	1389
3	0.2603	1384
4	0.2604	1383
5	0.2558	1429
6	0.2617	1370
7	0.2549	1438
8	0.2561	1426
9	0.2639	1350
10	0.2590	1393
11	0.2612	1372
12	0.2633	1352

Appendix C - Procedure for a Shock Tube Experiment

The following are the steps to perform a shock tube experiment after a sample mixture (in this case toluene/argon mixture) is prepared, and the aluminum diaphragm is annealed for 2 days at 623 K. The steps can be followed by looking at Fig. C1 where a schematic picture of the shock tube is shown.

- Insert diaphragm into shock tube diaphragm assembly (Section A) and turn on plunger magnet (at B)
- Evacuate the whole shock tube to 1.32×10^{-6} atm
- Once shock tube is evacuated close valve C, so the experimental section is isolated. Also close ball valve (D) in test section.
- Fill up test section with sample mixture to desired pressure P_1.
- Fill up the rest of the experimental section with pure argon to pressure P_1.
- Close gauge 1 in experimental section.
- Close valve E and fill up driver section with helium to desired pressure P_4.
- Once shock tube is ready, close all valves and perform the following in the shortest period of time possible:
  1. Open ball valve D in the test section
  2. Turn off the magnet (switch B) to rupture diaphragm
  3. Close ball valve D again.
- Record final pressure P_5 in gauge 4, time for shock wave to travel between transducers (at F), get a pressure history picture from oscilloscope (at G), and then wait three hours before collecting solid and gaseous samples.

Fig. C.1. Schematic Representation of the Shock Tube.


25 LITERS
DUMP TANK
BALL VALVE
VACUUM PUMP
E
LOW PRESSURE GAUGE
1
BALL VALVE
O-SCOPE
G
TIMER
F
PRESSURE TRANSDUCERS
PLUNGER
B
A
C
VACUUM SYSTEM
D

Appendix D - Determination of Cooling Rates

The determination of cooling rates in the present study was performed following the procedure described and applied to the thermal decomposition of Fluoroform by Tschuikow-Roux.[45,46] The use of this procedure is described for first order and an extension to bimolecular reactions is straight forward. The main steps of this procedure are now outlined.

Since the expansion wave in the driver section is isentropic and reversibly adiabatic, then

$$\frac{P(t)}{P_5} = \left(\frac{T(t)}{T_5}\right)^{\gamma/(\gamma-1)} \tag{D.1}$$

where γ is the specific heat ratio. Differentiating Eq. (D.1) with respect to time and setting $T(t) = T_5$, the initial cooling rate is obtained as a negative quantity

$$m = \left(\frac{dT}{dt}\right) = \left(\frac{\gamma-1}{\gamma}\right) \frac{T_5}{P_5} \left(\frac{dP}{dt}\right) \tag{D.2}$$

The rate of change of the pressure (dP/dt) is assumed to be a constant thus

$$P(t) = P_5 + (dP/dt)(t-t_1) \tag{D.3}$$

where 't' is time. By setting

$$\Delta T = T_5 - T(t) \tag{D.4}$$

and $$\frac{\Delta T}{T_5} \cong \frac{-m}{T_5} (t-t_1) \qquad (D.5)$$

which are obtained from Eqs. (D.1) through (D.3), and inserting them into the equation for the rate of disappearance of reactant 'N' during the cooling process

$$\frac{-dN(t)}{dt} = N(t)A \exp(-E/RT(t)) \ . \qquad (D.6)$$

the relative loss of reactant during the cooling process can be written as

$$\ell n \left(\frac{N_1}{N_2}\right) = -K_c \ \varepsilon \ , \qquad (D.7)$$

where $$K_c = A \exp(-E/RT_5) \ , \qquad (D.8)$$

and $$\varepsilon = \frac{R}{E} \frac{T_5^2}{m} \left(1 - \exp\left(-\frac{E}{R} \frac{\Delta T}{T_5^2}\right)\right) \ . \qquad (D.9)$$

N_1 is the number of moles at the start of the cooling process (at t_1), and N_2 is the number of moles at time 't_2' when the temperature has decreased to a specific value. In Eq. (D.9) Tschuikow-Roux defines ΔT at $t = t_2$ from Eqs. (D.4) and (D.5) as

$$\Delta T = \frac{2 \ T_5^2}{\left[2T_5 + \frac{E}{R\ell n10}\right]} \qquad (D.10)$$

For a first-order reaction we have that

$$\ln (N_1/N_o) = -K_c t_1 \tag{D.11}$$

and

$$\ln(N_2/N_o) = K_{un}\, t_1 \tag{D.12}$$

where the subscripts 'c' and 'un' mean corrected and uncorrected rate constants. Also, from logarithmic properties

$$\ln (N_1/N_o) = \ln(N_2/N_o) + \ln (N_1/N_2)$$

and from Eq. (D.7) have

$$\ln(N_1/N_o) = \ln (N_2/N_o) - K_c\, \varepsilon \ . \tag{D.13}$$

Combining Eqs. (D.11) through (D.13) the cooling rate correction is obtained as

$$K_c = (1 - \varepsilon/t_1)^{-1}\, K_{un} \tag{D.14}$$

Determination of Overall Reaction Rate Constant

The procedure to determine the reaction rate constant was performed assuming first order behavior found from reaction time studies. From the experimental data an initial least squares fit was performed on the variables 1/T vs log K_1 where

$$\log K = \log A - \frac{E}{2.303RT} \tag{D.15}$$

and

$$K = Ae^{-E/RT} \tag{D.16}$$

E = energy of activation,

A = preexponential term,

T = temperature,

R = universal gas constant.

This least squares produced an energy of activation and an uncorrected rate constant K_{un}. By applying Eq. (D.14) a new and corrected rate constant K_c was computed. This new K_c was compared to the old value K_{un} and a few iterations yielded the computed value of

$$K = 2.5 \times 10^6 \exp(-107 \text{ (kJ)}/RT) \text{ sec}^{-1}$$

with a correlation coefficient of $r^2 = 0.8636$ for the temperature range 1100-1700 K.

These calculations were computed by a Basic language program in a HP9816 computer which is shown in Fig. (D.1).

Fig. D.1. Computer Program Listing of Cooling Rate Calculations.

```
1     !!!!
```

```
212                 END IF
213       CALL Secant(Fold,Order,Ki[),Oweli(I),Initial(I),Ee(I))
214       K(I)=Fold
220   NEXT I
230   Rr2=R2
232   PRINT R2,H
233   H=H+1
240   IF R2<Eps THEN GOTO 189
250   FOR I=I TO N
260       Inver(I)=Inver(I)/.000I
270   NEXT I
271   PRINTER IS I
273   INPUT "DO YOU NANT TO TRANSFER DATA INTO ASCII FILES ? (Y=I/N=0)",Prb
274   IF Prb=0 THEN GOTO 290
280   CALL Trans(Inver($),Logo($),N)
290   PRINT
300   A=I0^A
301   PRINTER IS I
310   PRINT "  Ea(J/moI)            PREEXP.              R2             RATE ORDER"
320   PRINT Energy(H-1),Preex(H-1),Rcoeff(H-1),Order
321   PRINTER IS 1
330   END
340   !!!!
```

```
681  MASS STORAGE IS ":HP82901,700,0"
682  ALLOCATE Data$[255]
683 Format:   IMAGE 2X,60.60,2X,60.60,2X,3D
684  INPUT "WHAT IS THE NAME OF YOUR ASCII FILE?",Name$
685  INPUT "DO YOU WANT TO CREATE A NEW FILE? (Y=1,N=0)",Prb1
686  IF Prb1=0 THEN GOTO 705
692  CREATE ASCII Name$,N
693  ASSIGN @Path_1 TO Name$
694  ASSIGN @Path_2 TO BUFFER [256]
695  FOR I=1 TO N
696      OUTPUT @Path_2 USING Format;X(I),Y(I)
697      ENTER @Path_2;Data$
698      OUTPUT @Path_1;Data$
699  NEXT I
700  ASSIGN @Path_1 TO *
701  ASSIGN @Path_2 TO *
702  PRINT "YOUR X-Y VALUES HAVE BEEN FILED!!!"
703  GOTO 731
704  INPUT "HOW MANY DATA PTS. ARE ALREADY FILED?",N
705  ASSIGN @Path_1 TO Name$
706  ASSIGN @Path_2 TO BUFFER [256]
707  FOR I=1 TO N
708      ENTER @Path_1;Data$
709      OUTPUT @Path_2;Data$
710      ENTER @Path_2 USING Format;X(I),Y(I)
711  NEXT I
712  ASSIGN @Path_1 TO *
713  ASSIGN @Path_2 TO *
714  INPUT "HOW MANY NEW X-Y VALUES ARE YOU ENTERING?",N
715  PRINT "INPUT X-Y VALUES"
716  FOR I=1 TO N
717      INPUT X(I+M),Y(I+M)
719  NEXT I
720  M=N+M
721  PURGE Name$
723  GOTO 693
731  SUBEND
741  !
751  !
761  !
2824 SUB Progr(A,Res)
2834 Res=1
2854 SUBEND
2864 !
2874 !              SECANT METHOD (ROOT FINDER)
2884 !
3864 SUB Secant(Fold,Order,Kk,OwellI,InitialI,Eee)
3874 Epsl=.01
3875 Ao=Kk#10.I/10
3876 Aoo=Kk$1000/10
3884 Ii=0
3894 Tal=Ao/Aoo
3904 Aa=Ao
3914 Ard=Tal/Ao
3926 A=Aoo
```

```
3929  GOSUB 4100
3930  Fold=Res
3932  A=Aa
3933  GOSUB 4100
3934  New=Res
3954  IF Fold=New THEN GOTO 4015
3955  Tel=-New*Tel/(New-Fold)
3956  Aa=Aa+Tel
3964  Tel=ABS(Tel)
3974  IF Tel<Epsl THEN GOTO 4015
3984  Ii=Ii+1
3985  PRINT Ii,Tel
3994  Fold=New
4004  IF Ii=50 THEN GOTO 4034
4005  GOTO 3932
4015  Ed=1
4024  GOTO 4064
4034  PRINT "ITERATION LIMIT REACHED, I=50"
4044  GOTO 4064
4054  PRINT "STOP ITERATIONS DUE TO LARGE AO-AOO VALUE"
4064  GOTO 4410
4100  One=A
4101  Uno=(Initial1^(Order-1))*Owell1*(A-Kk)*(Order-1)
4200  Two=LOG(Uno)/(Eee*(Order-1))
4300  Res=One-Two
4400  RETURN
4410  SUBEND
5873  SUB Progr(A,Res,Order,Kk,Owell1,Initial1,Eee)
5874  One=-LOG(A)
5875  Two=LOG((Initial1^(Order-1))*Owell1*(A-Kk)*(Order-1))/(Eee*(Order-1))
5883  Res=One+LOG(Two)
5903  SUBEND
```

Appendix E: Computer Programs

The analysis of the experimental data was performed with the use of an HP/9816 computer in Basic language. A brief explanation of the computer program follows next and a print out of the program can be found in Fig. (E.1).

Also, the sensitivity analysis discussed in Section 3.3.2 was performed by a computer program written in Fortran for a mainframe IBM/370 computer. The description of this program (DGEAR) can be found in the IMSL routine handbook, and a printout of the program can be found in Fig. (E.2).

Reduction of Experimental Data

The Basic program (Fig. E.1) for data reduction was divided into three cases: 1) Perkin-Elmer analysis for C_5 and C_6 compounds, 2) Carle, for C_1 through C_4 compounds, and 3) Tracor, for products with molecular weight higher than toluene. The program requires the information shown in Fig. E.1(a) for Carle and Perkin-Elmer data. The measured areas from the gas chromatographs (GC) is then analyzed by the program using the equation

$$u_s = \text{Area}_s \times \left(\frac{C}{\text{Area}}\right)_c \frac{MW_c}{MW_s} \frac{P_f}{P_1} \qquad \text{(E.1)}$$

where u_s is the concentration of sample, Area_s is the area of the sample from GC, C_c is the concentration of known standard, Area_c is area of known standard, P_1 and P_f are the initial and final pressures in the

test section, and MW is the molecular weight of C = standard, or S = sample. Toluene decomposition is calculated from the equation

$$\frac{n_f}{n_1} = \frac{\text{Area(s)}}{\text{Area(mix)}} \frac{P_f}{P_1} \qquad \text{(E.2)}$$

where Area(s) is the area of toluene from sample bottle, and Area(mix) is the area of toluene from Ar/C_7H_8 mix bottle. For the case of Tracor data, only three compounds (biphenyl, bibenzyl, and Diphenyl Methane) were analyzed quantitatively. This analysis was performed by first obtaining a relation between the compound area in the liquid chromatograph as a function of the concentration. Once this relationship was found for the three compounds, the results were fed into the computer program which then calculated the compound concentration from a given area in a sample.

An example of the computer output is shown in Fig. E.1(b) where the concentration for each compound from the Perkin-Elmer and Carle G.C. is obtained. The program was also capable of storing all the data in disc files automatically and simultaneously for a given shock wave. This was of advantageous use when temperature-concentration plots were to be performed because plot programs were written in a way that permitted retrieving the whole file from a magnetic disc.

Modeling of Experimental Data

As it was mentioned earlier, the modeling of the experimental data was performed by using an IMSL routine called DGEAR which uses a backward differentiation formula, usually called Gear's stiff method, to

solve the set of simultaneous differential equations. The program printout is shown in Fig. (E.2). The program was modified so that in the output a concentration-time plot would be provided where the transient history of each species could be observed. The input parameters needed by the program were: reaction time, initial species concentration, number of steps in first iteration, accuracy of result for each iteration, and temperature. Also, the program has two subroutines (RTCNST and FCN) where the rate constants and the differential equations are input by the user.

Fig. E.1. Computer Program for Analysis of Experimental Data.

(a) Input Data for Program

(b) Output Results from Program

(c) Program Listing

SHOCK-WAVE DATA SHEET

Run No._____ Temp. T5'_____K Pf_____Psig

P1_____Torr P4_____Psig Dwell Time_____msec Date_____

PERKIN-ELMER

SAMPLE AREAS

_____ Range: X_____

_____

_____

_____

3.58_____

6.17 _____

CALIBRATION

Cyclohexane:_____ X_____

C6H6 (1083 PPM):_____

X_____

Toluene Mix: _____X_____

CARLE

CH4(4.80) _____

C2H4(5.85) _____

C2H2(8.10) _____

C3H6(9.12) _____

Propadiene(12.00) _____

C3H4(17.95) _____

1,3 Butadiene(20.90) _____

C4H4(25.50) _____

C4H2(35.70) _____

Range X_____

Can Mix 54:

CH4(4.92) _____

C2H2(8.39) _____

C3H6(9.12) _____

C3H4(18.46) _____

Range X_____

(a)

SHOCK NUMBER:85110703 TEMPERATURE: 1681

CARLE DATA

SAMPLE	AREAS	% FINAL/INITIAL RATIO
CH4(4.80)	4.39120	.39401
C2H4(5.85)	1.13290	.04676
C2H2(8.10)	83.32280	3.70556
C3H6(9.12)	0.00000	0.00000
PROPADIENE(12.00)	.76600	.02356
C3H4(17.95)	2.17960	.06703
1-3 BUTADIENE(20.90)	1.88350	.01213
C4H4(25.50)	1.16910	.00782
C4H2(35.70)	.42810	.00298

PERKIN-ELMER DATA

PI(ACTUAL)	PF(ACTUAL)	TOLUENE DECOMP.	%INITIAL TOLUENE COMP.
196.7586	18.7863	.2250	.7056

INITIAL CONC.(mol/mlts)	FINAL CONC.(mol/mlts)
7.470E-08	1.681E-08

TIME	AREA	% FINAL/INIT. RATIO
3.58	5.5180	.3281
6.17	40.3220	22.4988

(b)

```
1     OPTION BASE 1
10    !!!!
```

```
269  Ans=0.
270  Cccc=0.
272  IF Nueber=2 OR Nueber=4 THEN GOTO 570
273  IF Nueber=3 THEN GOTO 1022
274  !!!!
```

```
481  NEXT I
483  FOR I=1 TO 3
484  PRINT
485  NEXT I
486  IF Number=4 THEN
487             PRINT USING "5X,15A,80,5X,14A,40*;"  SHOCK NUMBER: ",Num,"TEMPERATURE: ",T5
488             PRINT
489             END IF
490  PRINT "                                CARLE DATA"
491  PRINT
492  PRINT "               SAMPLE            AREAS     % FINAL/INITIAL RATIO/CWELL"
493  PRINT
500  FOR I=I TO 9
520      PRINT USING "10X,20A,2X,4D.50,7X,20.50*;Carl$(I),Carle(I),C(I)
530  NEXT I
531  IF Ans=1 AND Number=4 THEN GOTO 903
532  INPUT "DO YOU WANT A COMPLETE PRINTOUT? (Y=1,N=0)",Ans
537  IF Ans=I AND Number=4 THEN
538                      PRINTER IS 701
539                      GOIO 483
540                      END IF
543  IF Number=4 IHEN
544             PRINTER IS 1
546             GOTO I343
547             END IF
548  !!!!
```

```
775  Perkin(8)=(Perkin(8)/(Toluene))*100
780  PRINT
790  PRINT
800  PRINT "INPUT THE FINAL SHOCK TUBE PRESSURE (PSIG)"
810  PRINT "AND THE INITIAL REGION 1 PRESSURE (TORR)"
820  INPUT Pf,P1
830  Pf=(Pf*1.03625)-1.93867
840  P1=(P1*.891901+45.12204
850  A=Pf+14.7
860  B=P1*.01934
863  Ed=A/B
870  Rat=Parea(9)*Ed/To1
871  Opdt=(P5-P1)*1000/T12
872  Tolinit=Toluene*P1*5.3807E-10
873  Tolfin=Tolinit*Rat
875  K1=-1000*LOG(Rat)/Dt
876  Dt=Dt*.001
878  INPUT " DO YOU WANT TO TRANSFER DATA FOR RXN ORDER CALCULATIONS? (Y=1,N=2)",Prb2
879  IF Prb2=1 THEN
880           INPUT "PRINT 'RXORDER' AT THIS TIME",Name$
881           CALL Rorder(Dt,T5,P5,K1,Dpdt,Tolinit,Tolfin,Name$)
882           END IF
883  PRINT "K1=";K1;"  DPDT=";Dpdt
884  Perkin(9)=Rat*100
885  FOR I=1 TO 10
890      PRINT
900  NEXT I
901  IF Ans=1 AND Number=4 THEN PRINTER IS 701
903  FOR I=1 TO 3
904  PRINT
905  NEXT I
906  PRINT "                          PERKIN-ELMER-DATA"
907  PRINT
908  PRINT
910  PRINT "            P1(ACTUAL)     PF(ACTUAL)   TOLUENE DECOMP.  %INITIAL"
911  PRINT "                                                          TOLUENE COMP."
913  PRINT
920  PRINT USING "13X,4D.4D,4X,4D.4D,8X,4D.4D,4X,DD.4D";P1,Pf,Rat,Toluene
921  PRINT
922  PRINT "            INITIAL CONC.(mol/slts)      FINAL CONC.(mol/slts)"
923  PRINT USING "18X,D.3DE,19X,D.3DE";Tolinit,Tolfin
930  PRINT
950  PRINT "                TIME       AREA     % FINAL/INIT. RATIO/DNELL"
951  PRINT
960  FOR I=0 TO 9
970      PRINT USING "13X,4D.2D,4X,4D.4D,4X,4D.4D";Time(I),Parea(I),Perkin(I)
980  NEXT I
981  IF Cccc=3 THEN
982           PRINTER IS 1
983           PRINT "END OF PROGRAM REACHED"
985           GOTO 1419
986           END IF
993  IF Number=2 THEN
994            INPUT "DO YOU WANT TO HAVE A PRINTOUT? (Y=1/N=0)",Ans
995            IF Ans=1 THEN
996                    PRINTER IS 701
```

```
997                     Cccc=3
998                     GOTO 903
999                     END IF
1000            END IF
1001  IF Ans=0 AND Number=2 THEN
1002          PRINT "END OF PROGRAM"
1003          GOTO 1419
1004          END IF
1006  IF Ans=1 AND Number=4 THEN
1007                    PRINTER IS 1
1009                    GOTO 1343
1010                    END IF
1011  IF Number=4 THEN
1012            PRINT "PUSH CONTINUE TO RESUME"
1014            PAUSE
1015            GOTO 279
1016            END IF
1018  !!!!
```

```
1192      Vect(I)=Bip(I)
1193  NEXT I
1194  X=Iyz(1)
1200  FOR I=16 TO 19
1203      IF I=18 THEN GOTO 1217
1204      CALL Loop(Aa,X,Vect(8),Pc(8),Pcc(8),M,G,I)
1205      PRINT "     A          B"
1206      PRINT M,G
1208      IF M=0 THEN
1209            PRINT " DEVIATION IS LARGER THAN 90% FOR ADJUSTING TRACOR CURVES"
1210            PRINT
1211            PRINT USING "51A,20.20,4A";" PROGRAM WAS COMPUTING CONCENTRATION FOR TIME = ",Tracar(I)," SEC"
1212            GOTO 1217
1213            END IF
1214      IF Traco(I)=0 OR Traco(I)=I THEN GOTO 1217
1215      Pot=(LOG(TracoII))-M)/G
1216      Co(I)=10^(Pot)
1217      H=I-14
1222      IF I=19 THEN GOTO 1238
1223      X=Iyz(N)
1225      IF I=16 THEN Aa=Iyz(N)-Gmath
1226      IF I=18 THEN Aa=Iyz(N)-Bihen
1228      IF I=16 THEN
1229            FOR J=I TO 5
1230                Vect(J)=Gmat(J)
1231            NEXT J
1232            END IF
1233      IF I=18 THEN
1234            FOR J=I TO 4
1235                Vect(J)=Bib(J)
1236            NEXT J
1237            END IF
1238  NEXT I
1239  FOR I=1 TO 21
1240      IF I=3 THEN GOTO 1243
1242      IracoII)=Traco(I)$Rr5/Barea
1243  NEXT I
1244  FOR I=1 TO 20
1245  PRINT
1254  NEXT I
1255  IF Ans=1 AND Number=5 THEN PRINTER IS 701
1257  FOR I=1 TO 3
1258  PRINT
1259  NEXI I
1260  PRINT "                              TRACOR DATA"
1261  PRINI
1264  PRINT "        TIME     AREA     CONC.(mol/ml) --      TIME      AREA      CONC.(mol/ml)"
1274  PRINT
1275  PRINT "                                T=150 C"
1277  Nn=1
1278  Na=2
1279  FOR I=Nn TO Na
1282  PRINT USING "6X,00.00,3X,0.30E,3X,0.30E,3X,8";Tracar(I),Traco(I),Co(I)
1283  NEXT I
1284  PRINT
1285  Nn=Na+1
```

```
IF Nn=9 THEN PRINT "                                T=220 C"
Na=Na+2
IF Na=23 OR Na<23 THEN GOTO 1279
IF Nuaber=5 THEN Rat=Rat+((14.5076*Traco(3)*Rr5)/(Trato1*Rr6*P1))
IF Cccc=4 THEN
          PRINTER IS I
          PRINT "END OF PROGRAN"
          GOTO 1417
          ENO IF
PRINT
IF Ans=I AND Nuaber=5 THEN GOTO 1318
IF Nuaber=5 THEN GOTO 1326
IF Nuaber=4 THEN
            PRINTER IS 1
            GOTO 1419
            ENO IF
INPUT "DO YOU NANT TO HAVE A PRINTOUT? (Y=1/N=0)",Ans
IF Ans=I ANO Nuaber=3 THEN
                      PRINTER IS 701
                      Cccc=4
                      GOTO 1257
                      END IF
IF Ans=I AND (Nuaber=1 OR Nuaber=4) THEN
                      PRINTER IS 701
                      GOTO 490
                      END IF
PRINT
PRINT
IF Ans=I AND Number=5 THEN PRINT USING "30A,DD.50";"          TOLUENE DECOMP. CORRECTED = ",Rat
PRINTER IS 1
IF Nuaber=5 THEN GOTO 1343
PRINT "ENO OF PROGRAN REACHED"
!
PRINT
IF Ans=1 THEN GOTO 1410
INPUT "DO YOU NANT TO NAVE A COMPLETE PRINTOUT? (Y=1/N=0)",Ans
IF Ans=I THEN
         PRINT "      LINE UP RIBBON TO PAPER, ANO PRESS CONTINUE NHEN READY"
         PAUSE
         PRINTER IS 701
         IF Nuaber=1 THEN GOTO 483
         IF Nuaber=2 THEN GOTO 903
         IF Nuaber=3 THEN GOTO 1257
         IF Nuaber=4 THEN GOTO 483
         IF Nueber=5 THEN GOTO 483
ENO IF
PRINT
!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!!
!
!              PREPARING DATA TRANSFERENCE TO ASCII FILES
!
INPUT "DO YOU NANT TO TRANSFER OATA INTO ASCII FILES?(Y=1/N=0)",Prb1
IF Prb1=0 THEN GOTO 1419
IF Prb1=1 THEN INPUT "ARE YOU CREATING NEW ASCII FILES?(Y=1/N=0)",Prb
IF Prb1=1 ANO Prb=0 TNEN
                INPUT "HON NANY OATA PTS. ARE ALREAOY IN FILE?",Chris
```

```
1348                N=Chris+1
1349                END IF
1350  IF Prb1=1 AND Prb=I THEN N=I
1351  !
1352  !               PREPARING PERKIN-ELMER DATA
1353  !
1354            FOR J=1 TO 9
1355                IF J=8 OR J=9 THEN
1356                            Asciii(N,J)=Perkin(J)
1357                            GOTO 1360
1358                            END IF
1359                Asciii(N,J)=Parea(J)
1360            NEXT J
1361  !
1362  !               PREPARING CARLE DATA
1363  !
1364            FOR J=10 TO 18
1365                Hh=J-9
1366                Asciii(N,J)=C(Hh)
1367            NEXT J
1368  !
1369  !               PREPARING TRACOR DATA
1370  !
1371            FOR J=19 TO 39
1372                IF J=19 THEN
1373                      Asciii(N,J)=0.
1374                      GOTO 1383
1375                      END IF
1376                IF J=34 OR J=35 OR J=37 THEN
1377                                        Hh=J-18
1378                                        Asciii(N,J)=Co(Hh)
1379                                        GOTO 1383
1380                                        END IF
1381                Jj=J-18
1382                Asciii(N,J)=Traco(Jj)
1383            NEXT J
1384  !
1385  !               REARRANGING DATA TO BE FILED
1386  !
1387  IF Prb1=1 AND Prb=1 THEN
1388        FOR J=8 TO 18
1391            Name$=Data$(J)
1392            Xxx(1)=T5
1393            Yyy(1)=Asciii(N,J)
1394            Zorro=1
1396            CALL Trans(Xxx(*),Yyy(*),Name$,Prb,N,Zorro)
1397        NEXT J
1398  END IF
1399  IF Prb1=1 AND Prb=0 THEN
1400            FOR J=8 TO 18
1403                Name$=Data$(J)
1404                Xx(N)=T5
1405                Yyy(N)=Asciii(N,J)
1407                CALL Trans(Xxx(*),Yyy(*),Name$,Prb,Chris,N)
1408            NEXT J
1409  END IF
```

```
1410  PRINT
1411  IF PrbI=0 THEN GOTO 1419
1412  !!!!
```

```
1631      Yy(I)=Ymean+(BI$(X(I)-Xmean))
1641 NEXT I
1642 GOTO 1664
1644 PRINT
1651 PRINT "VALUE R2 IS TOO LOW; THIS LEAST SQUARES TECHNIQUE IS NOT APPROPIATE"
1661 PRINT "    R2  "
1662 PRINT R2
1663 PRINT
1664 A=Ymean-(BI$Xmean)
1665 B=BI
1670 SUBEND
1671 !
1672 !            TRANSFERS DATA INTO FILES
1673 !
1675  SUB Trans(Xxx(*),Yyy(*),Name$,Prb,M,N)
1676  MASS STORAGE IS ":NP82901,700,0"
1677  ALLOCATE Data$[256]
1678 Format:  IMAGE 2X,6D.6D,2X,6D.6D
1681  IF Prb=0 THEN GOTO 1702
1687  CREATE ASCII Name$,M
1688  ASSIGN @Path_1 TO Name$
1689  ASSIGN @Path_2 TO BUFFER 256]
1690  FOR I=1 TO M
1692      OUTPUT @Path_2 USING Format;Xxx(I),Yyy(I)
1693      ENTER @Path_2;Data$
1694      OUTPUT @Path_1;Data$
1695  NEXT I
1697  ASSIGN @Path_1 TO *
1698  ASSIGN @Path_2 TO *
1699  PRINT USING "50A,X,10A";"YOUR X-Y VALUES HAVE BEEN TRANSFERRED TO FILE:",Name$
1700  GOTO 1722
1702  ASSIGN @Path_1 TO Name$
1703  ASSIGN @Path_2 TO BUFFER 256]
1704  FOR I=1 TO M
1705      ENTER @Path_1;Data$
1706      OUTPUT @Path_2;Data$
1707      ENTER @Path_2 USING Format;Xxx(I),Yyy(I)
1708  NEXT I
1709  ASSIGN @Path_1 TO *
1710  ASSIGN @Path_2 TO *
1711  PURGE Name$
1720  GOTO 1687
1722  SUBEND
1732  !
1742  !            AUXILIAR ROUTINE
1752  !
1762  SUB Loop(Aa,X,Vect(*),Pc(*),Pcc(*),M,B,I)
1772  Mad=5
1773  IF I=19 THEN Mad=4
1775  FOR Hh=1 TO 5
1776          IF I=16 THEN Pcc(Hh)=Pc(Hh+1)
1777          IF I=17 THEN Pcc(Hh)=Pc(Hh)
1778          IF I=19 AND Hh=5 THEN GOTO 1780
1779          IF I=19 THEN Pcc(Hh)=Pc(Hh)
1780  NEXT Hh
1792  Test1=ABS(Aa/X)*100
```

```
1762  SUB Loop(Aa,I,Vect(*),Pc(*),Pcc(*),N,G,I)
1796  IF Test1>5.0 THEN CALL Tracor(Aa,Vect(*),Pc(*),Pcc(*),M,G,Nad)
1797  IF Test1<5.0 AND I=16 THEN
1798                N=14.4380
1799                G=1.9840
1800                END IF
1801  IF Test1<5.0 AND I=19 THEN
1802                 N=15.47354
1803                 G=2.19098
1804                 END IF
1805  IF Test1<5.0 AND I=17 THEN
1806                 N=15.1193
1807                 G=2.1308
1808                 END IF
1810  SUBEND
1820  !
1830  !
1840  !
1850  SUB Rorder(Uno,Dos,Tres,Cuatro,Cinco,Seis,Siete,Name$)
1860  COM Ix(*),Y(*),Count(*),Z(*),F(*),Zz(*),Ff(*)
1870  MASS STORAGE IS ":HP82901,700,0"
1871  ALLOCATE Data$[255]
1872 Format:  IMAGE 2X,0.5D,2X,4D,2X,0.3DE,X,4D,2X,D.3DE,2X,D.3DE,2X,0.3DE
1873  Counter=1
1890  INPUT "DO YOU WANT TO CREATE A NEW FILE? (Y=1,N=0)",Prb
1900  IF Prb=0 THEN GOTO 2040
1911  N=1
1920  PRINT "INPUT OWELL(msec),T5',P5(Torr),K1,dP/dT,[X]G,[X]f"
1930  FOR I=1 TO N
1941      Ix(I)=Uno
1942      Y(I)=Dos
1943      Count(I)=Tres
1944      Z(I)=Cuatro
1946      F(I)=Cinco
1947      Zz(I)=Seis
1948      Ff(I)=Siete
1950      PRINT USING Format;Ix(I),Y(I),Count(I),Z(I),F(I),Zz(I),Ff(I)
1960  NEXT I
1970  CREATE ASCII Name$,N
1980  ASSIGN @Path_1 TO Name$
1981  ASSIGN @Path_2 TO BUFFER [256]
1990  FOR I=1 TO N
2000      OUTPUT @Path_2 USING Format;Ix(I),Y(I),Count(I),Z(I),F(I),Zz(I),Ff(I)
2001      ENTER @Path_2;Data$
2002      OUTPUT @Path_1;Data$
2010  NEXT I
2020  ASSIGN @Path_1 TO *
2021  ASSIGN @Path_2 TO *
2023  PRINT "YOUR X-Y VALUES HAVE BEEN FILED!!!"
2030  GOTO 2190
2040  INPUT "HOW MANY DATA PTS. ARE ALREADY FILED?",N
2041  N=1
2050  ASSIGN @Path_1 TO Name$
2051  ASSIGN @Path_2 TO BUFFER [256]
2060  FOR I=1 TO N
```

```
2061      ENTER @Path_1;Data$
2062      OUTPUT @Path_2;Data$
2070      ENTER @Path_2 USING Format;Ix(I),Y(I),Count(I),Z(I),F(I),Zz(I),Ff(I)
2080  NEXT I
2061  ASSIGN @Path_1 TO *
2082  ASSIGN @Path_2 TO *
2084  FOR I=1 TO N
2095  J=N+I
2097  Ix(J)=Uno
2098  Y(J)=Dos
2099  Count(J)=Tres
2100  Z(J)=Cuatro
2101  F(J)=Cinco
2102  Zz(J)=Seis
2106  Ff(J)=Sieta
2107  PRINT USING Foreat;Ix(J),Y(J),Count(J),Z(J),F(J),Zz(J),Ff(J)
2108  NEXT I
2109  PRINT
2110  PRINT
2111  N=N+N
2112  PRINTER IS 1
2113  FOR I=1 TO N
2114     PRINT USING Format;Ix(I),Y(I),Count(I),Z(I),F(I),Zz(I),Ff(I)
2115  NEXT I
2116  PRINTER IS I
2117  PURGE Name$
2118  GOTO 1970
2190  SUBEND
```

Fig. E.2. Computer Listing of DGEAR Modified Program.

FILE: TOLUENE FORTRAN A KANSAS STATE UNIVERSITY VM/SP CMS

```
      INTEGER IY,METH,MITER,INDEX,IWK(50),IER,K,INT
      REAL T,EPS,TMAX,H,TCALL
      EXTERNAL FCN,FCNJ
      DIMENSION Y(20),WK(500)
      COMMON DK(60)
      CHARACTER*1 ITITLE(76),CHAR(20) /'A','B','C','D','E','F','G','H',
     1  'I','J','K','L','M','N','O','P','Q','R','S','T'/
50    READ (5,1) IY,IK,ITITLE
      IF (IY.EQ.0) STOP
      READ (5,3) TEMP
      READ (5,2) MITER,INDEX
      READ (5,4) (Y(I),I=1,IY)
      READ (5,11) METH,INT,TMAX,EPS
      T=0.0
         H=TMAX/INT
      CALL RTCNST(TEMP)
      WRITE (6,5) ITITLE
      WRITE (6,22)
      WRITE (6,21) (I,DK(I),I=1,IK)
      IF (METH.EQ.1) THEN
         WRITE(6,30)
         WRITE(6,27)
         WRITE(6,29) H
      ELSE
         WRITE(6,30)
         WRITE(6,28)
         WRITE(6,29) H
      END IF
      WRITE(6,32) MITER
      WRITE (6,31) TMAX,EPS
      CMAX=Y(1)
      DO 500 I=2,IY
500   CMAX=AMAX1(CMAX,Y(I))
       ANORM=1.0/CMAX
      CALL GRAPH1 (0.0,TMAX,0.0,1.0,ITITLE,' ')
      DO 699 I=1,IY
699   CALL GRAPH2 (0.0,ANORM*Y(I),CHAR(I))
      WRITE (6,24) T
      WRITE (6,21) (J,Y(J),J=1,IY)
      INT=0
      TCAL=T
700   INT=INT+1
      TCAL=TCAL+H
      CALL DGEAR(IY,FCN,FCNJ,T,H,Y,TCAL,EPS,METH,MITER,INDEX,IWK,WK,IER)
          IF(IER.GT.128) GO TO 9999
          DO 9898 II=1,IY
 9898     Y(II)=(Y(II)*100/2.87E-07)
              WRITE (9,24) T
              WRITE (9,21) (J,Y(J),J=1,IY)
              WRITE (6,24) T
              WRITE (6,21) (J,Y(J),J=1,IY)
          IF(INT.GE.100.OR.T.GT.TMAX) GO TO 2000
      DO 1000 J=1,IY
1000  CALL GRAPH2 (T,ANORM*Y(J),CHAR(J))
      GO TO 700
```

```
FILE: TOLUENE  FORTRAN  A   KANSAS STATE UNIVERSITY VM/SP CMS

2000  WRITE (6,34) INT
      CALL GRAPH3
      GO TO 50
9999  CONTINUE
      WRITE (6,33)
      WRITE (6,25)IER,METH,MITER,INDEX
      WRITE (6,23)TCALL,H
      WRITE (6,21) (J,Y(J),J=1,IY)
      STOP
1     FORMAT (2I2,76A1)
2     FORMAT (2I2)
3     FORMAT (1E10.3)
4     FORMAT (5E10.3)
5     FORMAT (1H1,30X,'KINETIC MODELING PROGRAM',///,20X,76A1,///)
11    FORMAT (2I5,2E10.2)
21    FORMAT (5(I6,1PE16.5))
22    FORMAT (10X,'RATE CONSTANTS',/)
23    FORMAT(/,10X,'TCALL=',1PE12.5,'SEC',4X,'LAST H=',1PE12.5,'SEC')
24    FORMAT (//,21X,'AT TIME=',1PE13.5,/)
25    FORMAT(//,10X,'IER=',I3,'  METH=',I3,'  MITER=',I3,'  INDEX=',I3)
27    FORMAT (//,10X,'VARIABLE-ORDER ADAMS PREDICTOR CORRECTOR METHOD')
28    FORMAT (//,10X,'STIFF METHODS OF GEAR - DIFFERENCE FORMULAE')
29    FORMAT (/,10X,'FIRST STEP SIZE ',1PE12.5,' SEC')
30    FORMAT (/,10X,'VARIABLE STEP SIZE CALCULATION')
31    FORMAT (//,10X,'TMAX=',1PE12.5,'    EPS=',1PE12.5,'  RELATIVE ERRO
     1R OF BASIC METHOD',///)
32    FORMAT (//,10X,'ITERATION SCHEME #',I2,' APPLIED')
33    FORMAT (//,10X,'TERMINAL ERROR OCCURED- HELPFUL VALUES LISTED BELO
     1W',//,10X,'PLEASE CHECK ERROR PARAMETER [IER] FOR PROBABLE CAUSE')
34    FORMAT (//,10X,'NUMBER OF DATA POINTS IN TIME GRID=',I3,///)
      END
      SUBROUTINE RTCNST(T)
      COMMON DK(60)
      R1=8.31434*0.001
      R2=1.98545*0.001
      DK(1)=2.7*10**14.0*EXP(-73.4/(R2*T))
C     DK(2)=10**(9.3-(1.5/(2.3*R2*T*1000)))
      DK(2)=0.4*10**13.0*EXP(-3.7/(R2*T))
      DK(3)=0.0000760*EXP(-340.0/(R2*1000*T))*(T**5.5)
      DK(4)=8.3*10**17.0*EXP(-300.0/(R1*T))
      DK(5)=10**13.45*EXP(-16./(R2*T))
C     DK(6)=10**14.11*EXP(-76./(R2*T))
      DK(7)=10**13.66*EXP(-89./(R2*T))
      DK(8)=10**15.08*EXP(-32./(R2*T))
C     DK(9)=10**11.3*EXP(-51./(R2*T))
      DK(10)=2.82*10**12.0*EXP(-14.0/(R2*T))
      DK(11)=0.0
      DK(6)=0.0
      DK(9)=0.0
C     DK(12)=10**9.60*EXP(-8.2/(R2*T))
C     DK(13)=10**7.85*EXP(-10.0/(R2*T))
C     DK(14)=10**9.90*EXP(-17.1/(R2*T))
C     DK(15)=10**9.5*EXP(-20.8/(R2*T))
C     DK(16)=10**7.2*EXP(-9.2/(R2*T))
C     DK(17)=10**11.1*EXP(-53.6/(R2*T))
```

```
FILE: TOLUENE  FORTRAN  A   KANSAS STATE UNIVERSITY VM/SP CMS

C       DK(18)=10**8.9*EXP(-11.1/(R2*T))
C       DK(19)=10**9.6*EXP(-8.2/(R2*T))
C       DK(20)=10**11.5*EXP(-6.9/(R2*T))
        DK(21)=10**13.0*EXP(-16./(R2*T))
        DK(12)=0.0
        DK(13)=0.0
        DK(14)=0.0
        DK(15)=0.0
        DK(16)=0.0
        DK(17)=0.0
        DK(18)=0.0
        DK(19)=0.0
        DK(20)=0.0
        DK(22)=10**13.0*EXP(-80.0/(R2*T))
C       DK(22)=0.0
        RETURN
        END
        SUBROUTINE GRAPH1 (XMIN,XMAX,YMIN,YMAX,ITITLE,CHR)
        CHARACTER*1 C,CHR,ITITLE(76)
        DIMENSION OX(11),OY(11),C(51,101)
        DO 100 J=1,51
        DO 100 I=1,101
100     C(J,I)=CHR
        XSM=XMIN
        YBG=YMAX
        XSC=(XMAX-XMIN)*0.1
        YSC=(YMAX-YMIN)*0.1
        DO 200 I=1,11
        OX(I)=XMIN+XSC*(I-1)
200     OY(I)=YMAX-YSC*(I-1)
        XSC=10.0/XSC
        YSC=5.0/YSC
        RETURN
        ENTRY GRAPH2 (X,Y,CHR)
        RLY=YSC*(YBG-Y)+1.5
        RLX=XSC*(X-XSM) + 1.5
        IF (RLX.GE.102.0.OR.RLX.LT.1.0) RETURN
        IF (RLY.GE.52.0.OR.RLY.LT.1.0) RETURN
        C(INT(RLY),INT(RLX))=CHR
        RETURN
        ENTRY GRAPH3
        WRITE (6,600) ITITLE
        WRITE (6,601) OX
        WRITE (6,602)
        DO 300 I=1,51,5
        WRITE (6,603) OY(I/5+1),(C(I,J),J=1,101),OY(I/5+1)
        K1=I+1
        K4=I+4
300     IF (I.NE.51) WRITE (6,604) ((C(K,J),J=1,101),K=K1,K4)
        WRITE (6,602)
        WRITE (6,601) OX
        WRITE (6,600)
        RETURN
600     FORMAT (1H1,25X,76A1)
601     FORMAT (/,10X,11(1PE10.2),/)
```

```
FILE: TOLUENE  FORTRAN  A   KANSAS STATE UNIVERSITY VN/SP CNS

602   FORMAT (14X,'.+',20('....+'),'.')
603   FORMAT (2X,1PE10.3,'  +',101A1,'+ ',1PE10.3)
604   FORMAT (14X,'.',101A1,'.')
      END
       SUBROUTINE FCN(N,X,Y,YPRINE)
       DIMENSION Y(N),YPRIME(N)
       COMMON DK(60)
       YPRIME(1)=-DK(1)*Y(1)-DK(2)*Y(2)*Y(1)-DK(3)*Y(2)*Y(1)
     1 +DK(10)*Y(3)*Y(7)+DK(14)*Y(8)*Y(4)+DK(15)*Y(9)*Y(5)
     1 -DK(17)*Y(1)*Y(7)-DK(21)*Y(1)*Y(8)
       YPRIME(2)=-DK(2)*Y(2)*Y(1)-DK(3)*Y(2)*Y(1)+DK(1)*Y(1)
     1 -DK(5)*Y(2)*Y(4)+DK(7)*Y(4)+DK(9)*Y(6)+DK(10)*Y(3)*Y(7)
     1 -DK(11)*Y(4)*Y(2)+DK(12)*Y(5)*Y(7)+DK(13)*Y(4)*Y(5)+DK(14)*Y(8)*
     1 Y(4)+DK(15)*Y(9)*Y(5)-DK(20)*Y(10)*Y(2)
       YPRINE(3)=-DK(4)*Y(3)*Y(3)-DK(10)*Y(3)*Y(7)+DK(3)*Y(2)*Y(1)
     1 +DK(21)*Y(1)*Y(8)
       YPRINE(4)=DK(2)*Y(2)*Y(1)-DK(5)*Y(2)*Y(4)-DK(6)*Y(4)
     1 -DK(7)*Y(4)-DK(11)*Y(4)*Y(2)+DK(12)*Y(5)*Y(7)
     1 -DK(13)*Y(4)*Y(5)-DK(14)*Y(8)*Y(4)-DK(16)*Y(8)*Y(4)
     1 +DK(17)*Y(1)*Y(7)
       YPRIME(5)=DK(5)*Y(2)*Y(4)-DK(7)*Y(4)-DK(18)*Y(5)*Y(9)
     1 -DK(8)*Y(5)+DK(11)*Y(4)*Y(2)-DK(12)*Y(5)*Y(7)-DK(19)*Y(5)*Y(7)
     1 -DK(13)*Y(4)*Y(5)-DK(15)*Y(9)*Y(5)+DK(16)*Y(8)*Y(4)
       YPRIME(6)=DK(8)*Y(5)-DK(9)*Y(6)
       YPRIME(7)=DK(3)*Y(2)*Y(1)+DK(5)*Y(2)*Y(4)-DK(10)*Y(3)*Y(7)
     1 +DK(11)*Y(4)*Y(2)-DK(12)*Y(5)*Y(7)-DK(17)*Y(1)*Y(7)-DK(19)*Y(5)
     1 *Y(7)
       YPRINE(8)=DK(2)*Y(2)*Y(1)-DK(14)*Y(8)*Y(4)-DK(16)*Y(8)*Y(4)
     1 -DK(21)*Y(1)*Y(8)
       YPRINE(9)=-DK(15)*Y(9)*Y(5)+DK(16)*Y(8)*Y(4)+DK(17)*Y(1)*Y(7)
     1 +DK(19)*Y(8)*Y(1)+DK(21)*Y(1)*Y(8)
       YPRINE(10)=DK(13)*Y(4)*Y(5)-DK(20)*Y(10)*Y(2)
       YPRINE(11)=DK(4)*Y(3)*Y(3)+DK(6)*Y(4)+DK(8)*Y(5)+DK(22)*Y(12)
       YPRINE(12)=DK(4)*Y(3)*Y(3)-DK(22)*Y(12)
       RETURN
       END
       SUBROUTINE FCNJ(N,X,Y,PD)
       INTEGER N
       REAL   Y(N),PD(N,N),X
       RETURN
       END
```

Appendix F. Error Analysis

The calculation of the energy of activation (E_A) for the overall reaction rate as well as the product yield concentrations in the thermal decomposition of toluene were performed from a series of experimental measurements. Therefore, the estimation of error bars for these parameters should be performed using the propagation of error technique.

Experimental errors associated with other variables such as temperature, pressure and time can be found in Table F.1.

From the Arrhenius form of the reaction rate equation,[47] the energy of activation for toluene decomposition is:

$$E_A = RT(\ell n\ A - \ell n\ K). \tag{F.1}$$

where for first order reaction K is given by

$$K = -\frac{\ell n\ [T]/[T]_o}{t} \tag{F.2}$$

and R is the universal gas constant, A the frequency factor, T is the temperature, 't' the reaction time and $[T]$, $[T]_o$ are the final and initial toluene concentrations. The propagation of error equation for the standard deviation of K is given by.[48]

$$\sigma_K = \sqrt{\left(\frac{\partial K}{\partial [T]}\right)^2 \sigma^2_{[T]} + \left(\frac{\partial K}{\partial [T]_o}\right)^2 \sigma^2_{[T]o} + \left(\frac{\partial K}{\partial t}\right)^2 \sigma^2_t} \tag{F.3}$$

where the symbol σ_i means standard deviation of term 'i'. The standard deviations and partial derivatives expressions can be found in Tables F.1 and F.2

Similarly, the standard deviation of E_A is obtained from

$$\sigma_{E_A} = \sqrt{\left(\frac{\partial E_A}{\partial T}\right)^2 \sigma_T^2 + \left(\frac{\partial E_A}{\partial K}\right)^2 \sigma_K^2} \qquad (F.4)$$

where the term σ_K^2 from Eq. (F.3) is inserted into Eq. (F.4). In order to evaluate Eqs. (F.3) and (F.4) the following set of conditions was selected from the experimental data:

$$T = 1450 \text{ K}$$

$$[T_o] = 2.87 \times 10^{-7} \text{ mole/cm}^3$$

$$t = 2.0 \text{ msec}$$

$$[T]/[T]_o = 0.27$$

Inserting these values into the previous equations a value of 33.06 sec^{-1} is obtained for the deviation of the constant (corresponding to 5.05% deviation) and a value of 2.5 kJ/mole is obtained for the energy of activation which corresponds to a 2.3% deviation.

Thus, by the assumption of normal distribution 95% of the values of E_A will be bounded by:

$$E_A = 107 \pm 4 \text{ kJ/mole} \qquad (F.5)$$

The procedure for the product yields normalized to one millisecond is similar to the previous one. In this case the equation used is

$$\mu = \frac{X_f}{X_I} \frac{P_f}{P_I} \frac{1}{t} \text{ (\%/sec)} \qquad (F.6)$$

where the ratio X_f/X_I represents the initial (I) toluene composition, and the final (f) product yield, P_f is the final pressure, P_1 is the initial pressure, and t is the reaction time. The standard deviation for u is given by

$$\sigma_u = \left[\begin{array}{l} \left(\frac{\partial u}{\partial X_f}\right)^2 \sigma_{X_f}{}^2 + \left(\frac{\partial u}{\partial X_I}\right)^2 \sigma_{X_I}{}^2 + \left(\frac{\partial u}{\partial P_f}\right)^2 \sigma_{P_f}{}^2 \\ + \left(\frac{\partial u}{\partial P_I}\right)^2 \sigma_P{}^2 + \left(\frac{\partial u}{\partial t}\right)^2 \sigma_{t^2} \end{array} \right]^{1/2} \qquad \text{(F.7)}$$

The standard deviation and partial derivatives for the different terms are found in Tables F.1 and F.2. Using similar data as before and benzene yields at 1450 K a value of 1.13%/msec is obtained for the standard deviation which corresponds to a deviation of 11%. Therefore, the error bars associated with the results for the product yield curves is of 11%.

Table F.1. Standard Deviation of Measured Parameters

Parameter	Standard Deviation σ	Comment
t (time)	±0.1 msec	estimate from smallest division on oscillogram
P (pressure)	±10 torr (1.32×10^{-2} atm)	estimate from one-half of major division on gauge.
X_f, X_o	2.5×10^{-3}	*Calculated from g.c. analysis
T (temperature)	±35	*Calculated from reaction time study
[T], $[T]_o$	$\pm 7.18 \times 10^{-10}$ mol/cm^3	based on previous value of ±0.25% for X_f and X_o

*use equation $\sigma_X^2 = \dfrac{\Sigma x_i^2 - \dfrac{(\Sigma x_i)^2}{n}}{n-1}$

where: X_i = variable considered

n = number of replications

σ_x = standard deviation of variable x

Table F.2. Expressions for Partial Derivatives

$$\frac{\partial K}{\partial t} = \frac{\ell n\ [T]/[T]_o}{t^2}$$

$$\frac{\partial K}{\partial [T]_o} = + \frac{1}{t\ [T]_o}$$

$$\frac{\partial K}{\partial [T]} = \frac{-1}{t\ [T]}$$

$$\frac{\partial\ E_A}{\partial T} = R(\ell n\ A = \ell u\ K)$$

$$\frac{\partial\ E_A}{\partial K} = \frac{RT}{K}$$

$$\frac{\partial u}{\partial t} = - \frac{1}{t^2} \frac{X_f}{X_I}$$

$$\frac{\partial u}{\partial X_f} = \frac{1}{t\ X_I}$$

$$\frac{\partial u}{\partial\ X_f} = - \frac{1}{t\ X_I}$$

$$\frac{\partial u}{\partial\ X_I} = - \frac{X_f}{X_o^2}$$

Appendix G - Experimental Data

In this appendix, experimental data for shock waves run at 1.25% and 0.74% toluene composition are shown in Tables G1 through G3. First, the data for shock wave parameters calculated from shock wave relations discussed in Chapter 2 (Experimental Procedure). These are shown in Tables G1 (for 1.25×10^{-2} initial toluene mol fraction) and G2 (for 7.4×10^{-3}). Then Table G.3 shows all the normalized product yields per initial toluene concentration obtained from chromatographic and computer analysis of raw data.

Table G.1. Shock Datafor toluene initial mol fraction of 1.25×10^{-2}

Shock	Uncorrected Reaction Time (msec)	T_5 (K)	P_5 (atm)	$[C_7H_8]/[C_7H_8]_o$
85 050501	1.20	1255	9.2	0.7586
050901	1.30	1409	11.7	0.3346
050902	1.35	1366	11.2	0.5130
051001	1.35	1333	10.8	0.5186
051301	1.54	1386	11.4	0.4226
051302	0.90	1284	11.4	0.8808
061101	1.20	1115	10.9	0.7443
061201	1.00	1016	9.3	0.7856
061301	1.00	1149	11.4	0.7839
070601	0.70	977	11.8	0.8405
071101	1.00	963	10.4	0.8175
071701	1.45	1358	10.7	0.6727
071702	1.60	1301	10.7	0.7173
071802	0.70	1306	8.8	0.8397
080901	1.00	817	8.2	0.8194
100201	1.40	1337	8.8	0.6416
100202	1.30	1320	7.6	0.7010
100203	1.85	1575	9.9	0.1870
100401	1.80	1514	9.4	0.2350
100601	1.80	1524	9.5	0.1857
100701	1.40	1461	9.6	0.3011
100702	1.40	1418	8.9	0.3940
100703	1.40	1446	9.1	0.2694
100901	1.80	1501	10.0	0.2575
100902	1.20	1320	11.3	0.7051
100903	0.95	1149	9.9	0.7706
101601	1.60	1493	9.2	0.1979
101602	1.20	1406	7.3	0.4160
101603	1.30	1564	9.8	0.2115
101801	1.50	1580	10.0	0.1790
102201	1.55	1553	9.7	0.1175
102202	1.60	1597	8.4	0.1663

Table G.2. Shock Data for Toluene Initial Mol Fraction of 7.4×10^{-3}

Shock	Uncorrected Reaction Time (msec)	T_5 (K)	P_5 (atm)	$[C_7H_8]/[C_7H_8]_o$
85 102801	1.35	1635	9.1	0.1418
102802	1.00	1388	9.3	0.5134
102803	1.35	1536	9.6	0.2467
102901	1.35	1308	9.8	0.6343
102902	1.15	1287	10.2	0.7883
110401	1.35	1516	9.8	0.2381
110402	1.25	1501	10.0	0.2434
110403	1.15	1443	10.2	0.3728
110501	1.35	1555	7.6	0.2421
110702	1.05	1332	11.1	0.6247

Table G.3. Experimental Product Yields Computed by GC's and Computer Programs.

Shock	T_5(k)	Corrected Dwell Time (msec)	(Product Yields/Initial Toluene Composition) per msec (%/msec)					
			CH_4	C_2H_2	C_2H_4	C_3H_6	Propadiene	C_3H_4
85 050501	1255	1.723	0.00	0.041	0.076	0.022	0.0	0
050901	1409	1.845	1.25	1.759	0.373	0	0.089	0.181
050902	1366	1.915	0.00	0.176	0.138	0	0.041	0.089
051001	1333							
051301	1386	2.100	0.55	1.021	0.263	0	0.084	0.151
051302	1284	1.431	0.00	0.045	0.081	0.021	0.026	0.044
061101	1115	3.525	0.00	0.000	0.000	0.005	0.008	0.007
061201	1016	3.341	0.00	0.000	0	0	0	0
061301	1149	3.385	0.00	0.003	0	0.004	0.101	0
070601	977	2.830	0.00	0.000	0	0	0	0
071101	963	3.397	0.00	0.000	0	0	0	0
071701	1358	2.023	0.00	0.391	0.123	0	0.045	0.096
071702	1301	2.175	0.00	0.255	0.112	0.020	0.035	0.066
071802	1306	1.198	0.00	0.026	0	0.006	0.021	0.028
080901	817	3.226	0.00	0.000	0	0	0	0
100201	1337	1.937	0.00	0.506	0.222	0.026	0.052	0.101
100202	1320	1.833	0.00	0.365	0.228	0.020	0.041	0.090
100203	1575	2.451	1.62	7.284	0.266	0	0.044	0.106
100401	1514	2.885	3.23	6.401	0.476	0	0.071	0.161
100601	1524	2.366	0.00	0.000	0	0	0	0
100701	1461	1.971	3.35	7.020	0.852	0.044	0.117	0.271
100702	1418	1.949	1.58	3.763	0.799	0.001	0.128	0.289
100703	1446	1.946	3.01	7.211	10.63	0.030	0.135	0.319
100901	1501	2.360	3.16	7.528	0.621	0	0.101	0.226
100902	1320	1.751	0.00	0.184	0.142	0.019	0.032	0.060
100903	1149	3.021	0.00	0.003	0	0.004	0.002	0.006
101601	1493	2.147	2.93	9.533	0.361	0	0.097	0.190
101602	1406	1.736	2.46	3.186	0.972	0.069	0.114	0.285
101603	1564	1.853	1.63	9.838	0.315	0	0.067	0.160
101801	1580	2.057	2.13	8.786	0.288	0	0.068	0.156
102201	1553	2.089	2.81	9.755	0.351	0	0.060	0.155
102202	1597	2.150	1.56	5.681	0.197	0	0.043	0.092
102801	1635	2.102	1.19	6.852	0.182	0	0.056	0.166
102802	1388	1.709	0.33	1.865	0.484	0.043	0.136	0.365
102901	1308	2.101	0.31	0.054	0.050	0	0.055	0.151
110401	1516	2.098	2.46	8.230	0.447	0	0.088	0.219
110402	1501	1.979	2.94	9.442	0.653	0	0.128	0.317
110403	1443	1.890	1.71	4.496	0.713	0.043	0.129	0.323
110501	1555	2.096	3.33	11.695	0.444	0	0.104	0.292
110702	1332	1.795	0.00	0.482	0.206	0.017	0.062	0.186

Shock	T_5(k)	Corrected Dwell Time (msec)	(Product Yields/Initial Toluene Composition) per msec (%/msec) 1-3 Butadiene	C_4H_4	C_6H_6	$*C_7H_8$	Bibenzyl
85 050501	1255	1.723	0	0	0.52	75.9	0
050901	1409	1.845	0.0178	0	4.79	33.5	0.0017
050902	1366	1.915	0.0113	0	1.97	51.3	0.0140
051001	1333						
051301	1386	2.100	0.0130	0	3.29	42.3	0.0177
051302	1284	1.431	0	0	0.61	88.1	0.0076
061101	1115	3.525	0.0039				
061201	1016	3.341	0	0	0	78.6	0.0014
061301	1149	3.385	0.0010	0.0017	0.03	78.4	0.0025
070601	977	2.830	0.0012	0	0	84.0	0.0007
071101	963	3.397	0.0013	0	0.07	81.8	0
071701	1358	2.023	0.0095	0	2.15	67.3	0.0026
071702	1301	2.175	0.0072	0	1.78	71.7	0.0008
071802	1306	1.198	0.0076	0	0.37	84.0	0.0050
080901	817	3.226	0	0	0.03	81.0	0
100201	1337	1.937	0.0131	0.0027	1.83	64.2	0.0001
100202	1320	1.833	0.0121	0.0025	1.43	70.1	0.0066
100203	1575	2.451	0.0061	0	1.12	18.7	0.0030
100401	1514	2.885	0.0080	0.0010	3.37	23.5	0.0031
100601	1524	2.366	0	0	1.48	18.6	0.0033
100701	1461	1.971	0.0189	0.0043	4.83	30.1	0
100702	1418	1.949	0.0317	0.0037	5.71	39.4	0.0007
100703	1446	1.946	0.0301	0.0059	5.17	26.9	0.0005
100901	1501	2.360	0.0114	0.0025	3.61	25.7	0.0010
100902	1320	1.751	0.0076	0.0025	0.91	70.5	0.0630
100903	1149	3.021	0.0016	0	0.03	78.4	0.0025
101601	1493	2.147	0.0102	0.0034	1.83	19.2	0
101602	1406	1.736	0.0349	0.0081	5.17	41.6	0.0089
101603	1564	1.853	0.0111	0.0058	1.19	21.1	0.0222
101801	1580	2.057	0.0070	0.0034	1.12	17.9	0.0048
102201	1553	2.089	0.0091	0.0076	1.37	11.7	0.0003
102202	1597	2.150	0.0061	0	1.41	16.6	0
102801	1635	2.102	0.0162	0.0	0.85	14.2	0
102802	1388	1.709	0.0673	0.0274	4.04	51.3	0
102901	1308	2.101	0.0239	0	1.09	63.4	0
110401	1516	2.098	0.0171	0.0059	1.61	23.8	0
110402	1501	1.979	0.0252	0.0170	2.78	24.3	0
110403	1443	1.890	0.0353	0.0045	5.16	37.3	0
110501	1555	2.096	0.0228	0.0105	2.43	24.2	0
110702	1332	1.795	0.0298	0.0191	1.89	62.5	0

Shock	T_5(k)	Corrected Dwell Time (msec)	Biphenyl	Diphenyl Methane
85 050501	1255	1.723	0	0
050901	1409	1.845	0.0013	0.0007
050902	1366	1.915	0.0077	0.0071
051001	1333			
051301	1386	2.100	0.0079	0.0081
051302	1284	1.431	12.4 E-5	0.0004
061101	1115	3.525		
061201	1016	3.341	0	0
061301	1149	3.385	0	0.0011
070601	977	2.830	0	0.0016
071101	963	3.397	0	0
071701	1358	2.023	0	0.0006
071702	1301	2.175	0	0.0003
071802	1306	1.198	6.8 E-5	0
080901	817	3.226	0	0
100201	1337	1.937	0	0.0004
100202	1320	1.833	4.5 E-5	0.0013
100203	1575	2.451	1.9 E-5	0.0066
100401	1514	2.885	1.8 E-5	0.0032
100601	1524	2.366	0.1 E-5	0.0045
100701	1461	1.971	0	0
100702	1418	1.949	0	0
100703	1446	1.946	1.2 E-5	0.0002
100901	1501	2.360	3.1 E-5	0.0003
100902	1320	1.751	4.5 E-5	0.0016
100903	1149	3.021	0.1 E-5	0.0011
101601	1493	2.147	0	0
101602	1406	1.736	2.9 E-5	0.0010
101603	1564	1.853	0.0011	0.0059
101801	1580	2.057	0.0022	0.0042
102201	1553	2.089	0.2 E-5	0.0004
102202	1597	2.150	0	0
102801	1635	2.102	0	0
102802	1388	1.709	0	0
102901	1308	2.101	0	0
110401	1516	2.098	0	0
110402	1501	1.979	0	0
110403	1443	1.890	0	0
110501	1555	2.096	0	0
110702	1332	1.795	0	0

Appendix H. Product Yield-Temperature Curves

In this appendix, the yield vs. temperature distribution curves for C_3, C_4, and high molecular weight products are shown. These are the minor products in toluene pyrolysis and they are: propyne, propadiene, propene, 1-3 butadiene, vinylacetylene, diacetylene, biphenyl, diphenyl methane, and bibenzyl.

Fig. H.1. Product Yield-Temperature Curves for Minor Products.

(a) Propyne Yield, Initial Toluene Mol Fraction (ITMF) = 0.74×10^{-2}

(b) Propyne Yield, ITMF = 1.25×10^{-2}

(c) Propadiene Yield, ITMF = 1.24×10^{-2}

(d) Propadiene Yield, ITMF = 0.74×10^{-2}

(e) Propene Yield, ITMF = 1.25×10^{-2}

(f) Propene Yield, ITMF = 0.74×10^{-2}

(g) 1,3 Butadiene Yield, ITMF = 1.25×10^{-2}

(h) 1,3 Butadiene Yield, ITMF = 0.74×10^{-2}

(i) Diacetylene Yield, ITMF = 1.25×10^{-2}

(j) Diacetylene Yield, ITMF = 0.74×10^{-2}

(k) Vinylacetylene Yield, ITMF = 1.25×10^{-2}

(l) Vinylacetylene Yield, ITMF = 1.25×10^{-2}

(m) Biphenyl Yield, ITMF = 1.25×10^{-2}

(n) Diphenyl Methane Yield, ITMF = 1.25×10^{-2}

(o) Bibenzyl Yield, ITMF = 1.25×10^{-2}

PROPYNE YIELD (%/msec)
.6
.55
.5
.45
.4
.35
.3
.25
.2
.15
.1
.05
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE T5' (K)

(a)

PROPYNE YIELD (%/msec)
.6
.55
.5
.45
.4
.35
.3
.25
.2
.15
.1
.05
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE TS' (K)

(b)

PROPADIENE YIELD (%/mass)
.2
.175
.15
.125
.1
.075
.05
.025
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE 'TS' (K)

(c)

PROPADIENE YIELD (X/mseo).
.2
.175
.15
.125
.1
.075
.05
.025
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE 'TS' (K)

(d)

PROPENE YIELD (X/msec)
.08
.07
.06
.05
.04
.03
.02
.01
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE T5' (K)

(e)

PROPENE YIELD (%/msec).
.08
.07
.06
.05
.04
.03
.02
.01
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE 'TS' (K)

(f)

1,3 BUTADIENE YIELD (%/msec).
.07
.06
.05
.04
.03
.02
.01
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE 'TS' (K)

(g)

1,3 BUTADIENE YIELD (X/mmol).
.07
.06
.05
.04
.03
.02
.01
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE T5' (K)

(h)

DIACETYLENE YIELD (%/msec)
.09
.08
.07
.06
.05
.04
.03
.02
.01
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE T5' (K)

(i)

DIACETYLENE YIELD (%/msec)
.09
.08
.07
.06
.05
.04
.03
.02
.01
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE T5' (K)

(f)

VINYLACETYLENE YIELD (%/msec)
.009
.008
.007
.006
.005
.004
.003
.002
.001
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE 'T5' (K)

(k)

VINYLACETYLENE YIELD (X/msec).
.04
.035
.03
.025
.02
.015
.01
.005
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE T5' (K)

(1)

BIPHENYL YIELD (%/msec).
.009
.008
.007
.006
.005
.004
.003
.002
.001
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE TS' (K)

(m)

DIPHENYL METHANE YIELD (%/msec)
.009
.008
.007
.006
.005
.004
.003
.002
.001
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE 'TS' (K)

(n)

BIBENZYL YIELD (%/msec)
.07
.06
.05
.04
.03
.02
.01
0
800
900
1000
1100
1200
1300
1400
1500
1600
1700
TEMPERATURE TS' (K)

(o)

Thermal Decomposition of Toluene at Intermediate Temperatures in the KSU Single Pulse Shock Tube

by

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B.S.N.E., Kansas State University, 1983

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ABSTRACT

A pyrolytic study of the thermal decomposition of vapor phase toluene diluted in argon was performed by using the KSU Single Pulse Shock Tube. The conditions in this study included a temperature range from 800 to 1700 K where only the portion from 1100 to 1700 K was considered further for analysis of product species. The initial toluene mol fraction in argon in the test section of the shock tube was varied from 0.74×10^{-2} to 1.25×10^{-2}. The reaction time was 1.97 ± 0.13 msec for the temperature range 1100 - 1700 K and initial toluene mol fraction of 1.25×10^{-2}, 2.01 ± 0.21 msec for 7.4×10^{-3} initial toluene mol fraction, and 3.25 ± 0.24 msec for the temperature range 800 - 1100 K and 1.25×10^{-2} toluene mol fraction. The reaction pressure (P_5) was varied from 10.5 to 20 atm. Analysis of the stable products was performed by using three gas chromatographs containing flame ionization detectors coupled to a computer data station that reduces the data.

The experimental results were divided into three categories: 1) reaction time study, 2) temperature effect studies, and 3) modeling of the experimental data. The reaction time study confirmed the conclusions from other authors that the toluene pyrolysis is a first order reaction. This conclusion was also drawn when the initial toluene concentration in argon was varied. The temperature studies provided different results from previous studies where the high yield of benzene were observed for the first time in low temperature shock tube studies. Other species observed were acetylene, methane, ethylene, and smaller concentration of propyne, propene, propadiene, 1,3 butadiene,

vinylacetylene, diacetylene, styrene, biphenyl, diphenyl methane, and bibenzyl. Other species present with high molecular weight were not identified and they included C_9, C_{10}, C_{18} compounds. The modeling of the experimental data was based on the product yield observations, and the tabulated values for reaction rate constants obtained from the literature.